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THE INSTITUTE OF PETROLEUM

AN Ordinary General Meeting of the Institute of Petroleum was held at 26 Portland Place, London, W.1, on 2 October 1957, the Chair being taken by The Rt. Hon. Lord Geddes, President of the Institute.

The General Secretary read the minutes of the previous meeting, which were confirmed and signed as a correct record. He also announced the names of members elected since the previous meeting.

The Chairman, introducing the authors of the papers to be presented, said: The first of the papers this evening is " Modern Trends in Petroleum Analysis," the authors being W. H. Thomas and Dr H. Powell. Mr Thomas needs little introduction, for he has been a member of the IP since 1920, and a member of Council for a number of years. He is deputy Chairman of the Standardization Committee and chairman of one of its sub-committees. He has been associated with the Sunbury Research Station since 1923, except for five years at Abadan and one year in New York.

Dr Powell has for several years been a member of the IP Hydrocarbon Research Group and is secretary and chairman of the Spectroscopic Panel of that Group. He first joined the BP group as development chemist at Llandarcy in 1938. Since 1941 he has been at the Sunbury Research Station and is at present in charge of analytical research as Assistant Head of the Analytical Section.

The second paper, " New Trends in the Instrumentation of Refinery Processes," by S. W. J. Wallis and D. S. Townend, will be presented by Mr Townend, as Mr Wallis is unfortunately indisposed.

Mr Townend gained some of his experience as an engineering officer in the Navy and with the English Electric Company. Subsequent to that, after joining the British Petroleum Company, he had a year at Cambridge.

The following papers were then presented in summary.

MODERN TRENDS IN PETROLEUM ANALYSIS*

By H. POWELL† (Fellow) and W. H. THOMAS† (Fellow)

SUMMARY

The purpose of this paper is to review the recent advances in methods for the examination of petroleum products and to indicate what the future trend in this direction is likely to be. Much of the work described has been done or is in progress in the BP research laboratories at Sunbury-on-Thames, but opportunity has been taken to include references to the results of investigations which have been made elsewhere, particularly in the U.S.A.

It is apparent that the most important trend is towards automatic physical methods of analysis, whereby much more information may be obtained in a fraction of the time required by the older well-tried procedures. In most cases the newer types of equipment are expensive, but their cost is easily offset against the increased amount of information obtained and the savings effected in refinery operation, notably the reduction in tanker delays and the overlong occupation of tanks whose contents cannot be moved until time-consuming analyses are completed.

INTRODUCTION

THE advances made by the petroleum industry, particularly during the last decade, have necessitated a parallel development of methods of analysis and quality assessment. It is since 1938 that the most marked advances have been made in analytical procedures, and even from a cursory study of U.K. and U.S. scientific publications it would appear that this development represents a very substantial proportion of the total petroleum research carried out over the last 18 years.

Considerable impetus was given to this branch of petroleum technology during the second world war because of the vastly increased demand for the highest grades of products and of the necessity for the development and large-scale production of specialized types of fuels and lubricants for combat aircraft, land vehicles, and ships. More recently, however, the advances made in means of transport and the demand of the petroleum chemical industry, together with the necessity for a much increased speed of analysis, have dictated the most modern trends in analytical research.

The developments considered in this paper fall into two main groups, one concerned with the broadest field of hydrocarbon and petroleum analysis, and the other with the use of instruments and instrumentation to reduce analysis time to a small fraction of that required by the classical chemical and physical procedures.

For analysis to play its proper part, its cost must be taken into account, and the cost is dependent on two main factors: the time occupied in each determination and the wages of the individual worker. If analysis is to be effective in the modern sense it must be economical and swift, and therefore to satisfy these requirements it must be based as far as possible on instrumentation.

In the refinery, tanker delays and the over-long occupation of tankage by finished products can often be caused by the necessity of waiting for analytical results, and such delays invariably represent the loss of

* MS received 30 January 1957.

† British Petroleum Co. Ltd.

very large sums of money. Modern instrumental procedures occupy only a very small fraction of the time required by the older well-established methods, and even if the cost of the instruments amounts to thousands of pounds, their installation and use can easily be justified by the elimination of losses due to delays in storage and shipment.

Petroleum analysis in research, development, and refinery operation is, as a whole, highly complex, and in order to present a picture of modern trends which can easily be appreciated it is proposed to sectionalize this review under a number of sub-headings.

MICRO CHEMISTRY

Although as will be seen in the following pages, instrumental methods are the main theme in this paper, they are not the only means available for obtaining analytical data on very small samples. In recent years micro chemistry has been applied successfully to petroleum analysis, and many of the conventional tests for petroleum can now be made on a micro scale. Micro methods, although less accurate, have been found to be appreciably speedier than the classical procedures (*e.g.* carbon and hydrogen content), and the Untersaucher method for oxygen content by combustion is noteworthy on account of its accuracy and convenience. Micro methods are usually more rapid, they require less bench space, and the equipment is cheaper and easy to make (apart from the cost of a very accurate balance), but they do require a high degree of skill and experience.

Methods have been developed [1, 2] whereby a reasonably complete assay may be made on very small geological samples of crude oil, and thereby data are obtained which would not have been thought possible five years ago. Practically the whole field of petroleum testing has been covered, the micro methods available ranging from those designed for analysing minute amounts of grease from faulty bearings [3, 4] to methods for determining flash point [5] and vapour pressure [4] on samples of less than 1 ml.

In spite of the speed of micro procedures, the greater care and manipulative skill required make it unlikely, with certain exceptions, that there will be any considerable change to micro methods for routine analytical purposes. Nevertheless, micro techniques allied to spectrographic examination will, in particular, open up the field of geochemistry, which has for so long been somewhat of a geological orphan.

CHEMICAL METHODS

The use of the most advanced chemical techniques in the petroleum industry has been confined to specific tasks, such as the determination of trace impurities. For example, a paper chromatographic method has been developed for the determination of lead concentrations in platformer feedstocks down to 10 parts per thousand million, the concentration of lead being estimated by the visual appearance of chromatograms in the form of magenta-coloured rings on filter paper. No complicated apparatus is required, and the method is considered to be a rapid one after experience in its use has been obtained. Trace amounts of lead in naphtha may also be determined by a colorimetric procedure.[6]

Colorimetric and spectrophotometric procedures are in fact in common use in the petroleum laboratories for many inorganic analyses. These techniques are also being used for the determination of certain additives, while a rapid method has been developed in the BP research laboratories for the determination of MEK contents of water above 0·05 per cent. In this the colour developed with sodium nitroprusside is matched with standards in a comparator, and the determination takes approximately ten minutes.

A new technique which has considerable scope in the determination of trace elements is that of radioactivation analysis.[7] The method involves irradiation of the sample, and then measurement of the radioactivity of the elements to be determined, usually after they have been isolated by chemical separations. For certain types of analysis, however, *e.g.* where the radioisotopes are gamma emitters and where the gamma rays emitted by the various radionucleids may be conveniently resolved, no prechemical separation is necessary. The advantage of the radioactivation technique lies in its extremely high sensitivity, which for many elements is far in excess of spectrographic techniques. It therefore seems attractive for geochemical work.

Other ways in which radioactivity, using radioactive isotopes, is being harnessed to problems in the petroleum industry have been reviewed in a recent paper by Putman.[8]

PHYSICAL METHODS

Spectrometry

Although, as a result of recent advances in instrumentation and techniques, radiation and mass spectrometry are well established for both routine and research analyses in the petroleum industry, the next few years will see an even greater contribution of these physical measurements to the analysis of petroleum and its products.

(1) *Infra-red.* In the field of absorption spectrometry, double-beam instruments are now available which, in a matter of minutes, automatically record infra-red and ultra-violet spectra in a form suitable for direct measurements to be made from them. These instruments have also considerably increased the scope of spectrometry in both qualitative and quantitative analyses; for example, the differential technique [9] of double-beam infra-red spectrometry has increased the power of detection and accuracy of the determination of minor components of a mixture

and in fact has made possible many analyses which could not otherwise have been done. This technique has already been applied successfully to many problems, among them the determination, on a routine basis, of anti-icing additives in gasolines and the analysis of insecticide blends.[10]

Another recent development in infra-red spectrometry has been the potassium bromide pressed-disk technique for the examination of solid materials.[11] Previously, infra-red spectra of materials solid at room temperature had to be obtained in solution or as a fine dispersion in a liquid medium. These procedures, however, suffer from the disadvantage that the solvent or dispersing medium itself has characteristic absorption, so that the resulting spectrum shows the absorption bands of the solvent or dispersing medium as well as those of the material under examination. In the pressed-disk technique the sample and potassium bromide are finely ground, thoroughly mixed, and then pressed at 20 tons/sq. in. into a disk of approximately 13 mm diameter and 1 mm thick. The potassium bromide is infra-red transparent, so that the spectrum obtained is that of the sample only. By this means, satisfactory spectra may be obtained on sample quantities of the order of 1 mg. In a modification of the procedure [12] the sample is dissolved in a suitable solvent and the solution sprayed on to the finely-ground potassium bromide. The solvent is then evaporated and the disk prepared in the usual way.

The infra-red examination of very small quantities of liquid is now possible with modern types of microcells, and the ability to obtain spectra on such small quantities, both in the liquid and solid states, will undoubtedly be of considerable value where very little sample is available, *e.g.* the examination of the components of engine exhausts. The use of microcells will also enable measurements to be made on the small fractions from vapour phase chromatographic columns and from micro-distillations.

Hitherto, in industrial laboratories infra-red spectroscopy has been in general confined to measurements in the 3–15-μ region, in which the absorption of hydrocarbons is associated with the fundamental stretching and deformation frequencies of the various carbon/carbon and carbon/hydrogen linkages. However, as a result of improved instrumentation, attention is now being paid in many laboratories to the 1–3-μ and 15–25-μ regions. It is expected that the 1–3-μ region will make useful contributions to structural and type analyses, as well as to quantitative individual component analyses, and it might well prove to be of value in the continuous analysis of liquid plant streams. As many of the C–S and S–S frequencies occur in the 15–25-μ region, this may have useful application to research work on sulphur compounds.

Apart from the determination of certain additives in lubricating oil, infra-red spectrometry has had little use in lubricating oil analysis. However, by comparing the used and fresh oils in the double beam unit, the differential spectrum obtained would be characteristic of the changes which have occurred in the oil during use. Luther [13] has indeed studied the oxidation of pure hydrocarbons and oils using this technique.

(2) *Raman Spectrometry.* Although Raman spectrometry has been used successfully in the analysis of hydrocarbon mixtures,[14] it is unlikely to have general application in the petroleum industry. Its main limitation is that it cannot be used for the examination of coloured samples, so that its application is limited to the lower boiling fractions of petroleum, and even in this region it offers no serious competition to mass and infra-red spectrometry.

(3) *Ultra-violet.* The trend in ultra-violet spectrometry is towards the extension of measurements to wavelengths below 2100 A, the lower limit of most present-day commercial spectrometers. The newer types of ultra-violet spectrophotometer, however, permit measurements down to 1860 A, and it is likely that the region 1860-2000 A could complement information obtained by other methods, particularly on mono-olefins and aromatic-type compounds. A further extension into the vacuum ultra-violet region would be even more fruitful, and work at King's College, London, supported by the Hydrocarbon Research Group of the IP, has resulted in the design of equipment which could well form the basis of a commercial instrument. The value of measurements in the region of 1650–2100 A for the determination of aromatics in lubricating oil fractions was demonstrated in a paper [15] presented by Burdett.

Another possible development in the ultra-violet range is that of introducing chromophoric groups (as in colorimetry) into non-absorbing compounds and then measuring the intensity of the absorption peak of the added group.

Ultra-violet spectrometers may also be useful in detecting the end points of non-aqueous titrations to which pH meters have limited application, due mainly to the high resistance in the system.

(4) *Mass Spectrometry.* During the past few years, mass spectrometry has become perhaps the most powerful analytical tool available for the examination of high molecular weight materials [16-18], and in this field an excellent summary of the capabilities of the mass spectrometer on heavy oil composition has been given by O'Neal.[19] The methods developed give molecular weight distributions and hydrocarbon-type composition and, as an example of this, Fig 1 shows graphically an analysis of finished wax of 138°–140° F melting point expressed as the amount of each hydrocarbon type present at each carbon number. For such an analysis, an accuracy of 1 per cent is claimed. Even more impressive is the information that can be

obtained on the composition of lubricating oils by a combination of physical separation procedures and mass spectrometric examination of the various fractions. An example of the data that can be

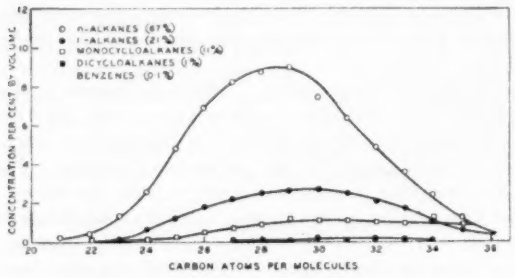

FIG 1

MASS SPECTROMETRIC ANALYSIS OF A PARAFFIN WAX

obtained is given in Table I, in which a hydrocarbon type analysis is given for two cuts from a thermal diffusion column of a 435 mol. wt. fraction of dewaxed saturates from Kuwait long residue.

There can be little doubt that this combination of physical separation, *e.g.* chromatography, distillation, and thermal diffusion, with mass spectrometry will yield a wealth of new information covering the composition of oils and waxes.

Although the mass spectrometer has, in the past, been used in a limited way for the identification of chemical structure, this type of application is now receiving much greater attention as a result of the work presented in a paper by Beynon.[20] However, to obtain the utmost information it is necessary to have sufficient resolution to make use of the precise values of the atomic weights of the elements instead of the integral multiples of unit mass commonly used in conventional analytical mass spectrometry.

TABLE I

Hydrocarbon Type Analysis for Two Cuts from Thermal Diffusion of Dewaxed Saturates from a Kuwait Long Residue

Hydrocarbon type	Composition—per cent by volume	
	Cut No. 1	Cut No. 5
Saturates:		
*iso*Alkanes	56	—
Monocycloalkanes	28	8
Dicycloalkanes	11	12
Tricycloalkanes	4	23
Tetracycloalkanes	1	20
Pentacycloalkanes	—	13
Hexacycloalkanes	—	8
Heptacycloalkanes	—	4
Octacycloalkanes	—	1
Mono-aromatics:		
Benzenes	—	4
Monocycloalkylbenzenes	—	6
Dicycloalkylbenzenes	—	1
Totals	100	100
Z — Number (in C_nH_{2n} + Z)	+0·7	−5·8

Reprinted from *Proc. Fourth World Petrol. Congr.*, 1955, Section V/c.

Other interesting developments in mass spectrometry are those involving methods of ionization other than that of electron impact used in all the existing commercial equipment. These include photoionization and field emission, which could well have useful application in quantitative analysis and in studies of chemical kinetics and surface chemistry. Both have the advantage that only molecular-ions are produced, so that the resulting spectrum is relatively simple. Further, in photoionization sources the energy may be such that only certain types of molecules are ionized. Lossing [21] has found that with a Krypton lamp only unsaturated hydrocarbons are ionized, so that for a mixture of olefins and paraffins the spectrum would be that of olefins only, with the result that very small concentrations of olefins could be readily determined. This selective type of ionization can also be achieved by a suitable choice of the electron accelerating voltage in conventional instruments, and a low voltage procedure has been developed,[22] using an electron accelerating voltage of between 9 and 10 volts, for the determination of unsaturateds in petroleum naphthas. This overcomes one of the limitations of conventional mass spectrometry when applied to cracked gasolines in that it cannot separate olefins from naphthenes.

(5) *Nuclear Magnetic Resonance.* One of the radio-frequency spectroscopic techniques developed since the war is that of nuclear magnetic resonance,[26] which is based on the observation that many atomic nuclei behave as though they possess a nuclear spin. When placed in a magnetic field, a number of energy levels become available to them, each level corresponding to a definite orientation of the nuclei relative to the field. Nuclear resonance spectra occur when transitions among these energy levels are induced by radio-frequency radiation, the frequencies of such radiation being characteristic of the atomic nuclei. Under high resolution, however, the precise frequency at which resonance occurs is dependent on the chemical environment of the nuclei, due in the main to local magnetic effects caused by surrounding electrons. Thus the proton resonance in CH_3, CH_2, and OH groups occurs at different frequencies, as will be seen from Fig 5, which gives nuclear magnetic resonance spectra of various organic compounds. Not all atomic nuclei exhibit this phenomenon, and the most abundant isotopes of carbon, oxygen, and sulphur (C^{12}, O^{16}, and S^{32}) have zero spin, and therefore give no nuclear magnetic resonance. However, due to the existence of proton resonance and the frequency shift known as the "Chemical Shift," caused by the particular environ-

ment of the proton in the molecular group, the technique provides yet another molecular "fingerprint" for hydrocarbons and other compounds. Various U.S. petroleum laboratories have already commenced work in this field using commercial equipment, Fig 2.

It is too soon to assess the full potentialities of this technique, but on the basis of the information at present available, it appears to be a most promising tool,[27] and will no doubt complement and supplement other spectroscopic and physical methods in qualitative, quantitative, and molecular structure analyses. It is even possible that the technique could be used for the continuous analysis of plant streams.

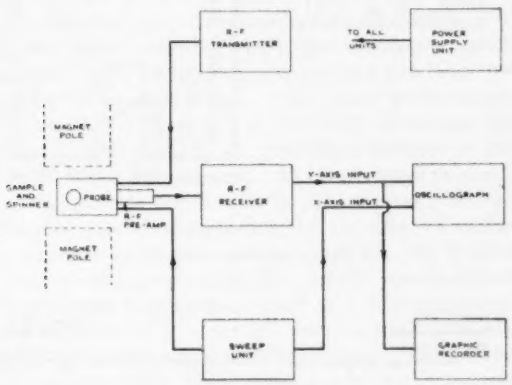

FIG 2

DIAGRAM OF HIGH RESOLUTION *n–m–r* SPECTROMETER EMBODYING AN ELECTROMAGNET

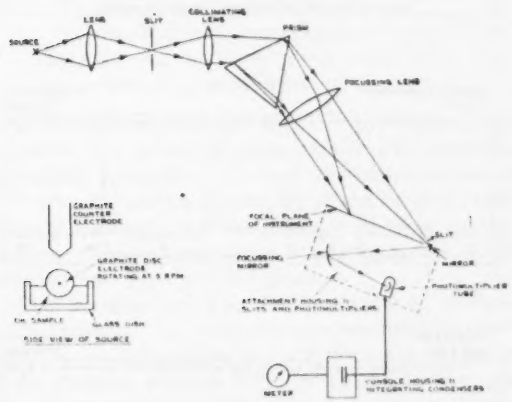

FIG 3

SCHEMATIC DIAGRAM OF THE HILGER MEDIUM QUARTZ DIRECT READING SPECTROMETER

(6) *Emission.* For many years after its introduction into the petroleum industry, emission spectroscopy was confined to the type of microgram analysis which had very little bearing on the quality of petroleum products. In fact, it performed those inorganic analyses which by chemical means were either too involved because of the complexity of the sample and therefore very time-consuming (*e.g.* crude oil ash analyses) or presented considerable difficulty because of the low concentrations of the elements of interest. In recent years, however, due to the use of additives in lubricating oils and the increased use of diesel engines, emission spectroscopy has ceased to be the Cinderella of the "petroleum-spectroscopy" family. Reliable methods of determining the additive elements in lubricating oils without recourse to ashing have been developed and, using a direct reading photoelectric attachment, Fig 3, an oil can be examined quantitatively for certain selected elements in approximately six minutes. The equipment can also be employed for the determination of iron in used engine oils as a means of assessing wear and will be of considerable value to refinery laboratories for checking the formulation of the blended oils in place of the time-consuming sulphated ash method at present in use.

It has been found that a spectrographic method of determining the concentration of the elements in used engine oils [23] provides a rapid and convenient means of assessing wear in diesel locomotive engines and of dictating the maintenance and overhaul programmes. This technique is now in general use in America, and will doubtless be extended to all countries in which diesel locomotion is used.

(6) *Flame Photometry.* Flame photometry, which has not had the recognition it deserves, is being used in many laboratories for various analyses, including the determination of sodium and TEL in gasoline, calcium in lubricating oil assays, and for the determination of sodium in catalysts and crude oil. The technique is highly sensitive to matrix effects, and if the sample being examined contains many elements preliminary chemical separation may be necessary. It is most useful when a large number of similar samples have to be analysed. A simple non-dispersive photometer is being used in the BP research laboratories for the determination of sodium in catalysts and in fuel and crude oils.

X-Rays

X-rays have found many useful applications to research programmes, but their most valuable contribution to petroleum analysis has undoubtedly been the provision of a rapid method for sulphur determination in the heavier products.[28] X-rays are absorbed quantitatively by sulphur, and this effect is the basis of an X-ray method for the very rapid determination of total sulphur in hydrocarbon distillates, crude oils, and residual fuels. The determinations take only a few minutes, compared with several hours by chemical methods, but are limited to materials of sulphur content greater than 0·05 per cent by weight. The X-ray absorption method is now being used on routine sulphur determinations in many refineries,

and in some it is coping with as many as 30 determinations per day. The technique may also be applied to TEL determinations.[29]

The analytical chemist is making ever-increasing use of the facilities offered by X-ray diffraction equipment, *e.g.* for the identification of the chemical composition of precipitates, a test for purity, and in the measurement of particle size. The recent publication of the ASTM card index of diffraction patterns has greatly extended and simplified the use of this "fingerprint" system. The modern unit consists of a high voltage X-ray transformer with precision control gear, including a wide range exposure timer and an all-metal X-ray tube with a fine adjustable focal point continuously effected by an automatic pumping plant. A wide variety of target materials providing a corresponding range of wavelengths is available, and a rotating anode type of unit may be used to provide more powerful beams of radiation of finer foci.

The technique of X-ray fluorescence spectrometry is analogous to that of optical emission spectroscopy, and it is expected that they will be found to be complementary one to the other. Many applications are known, the most noteworthy of which are the element analysis (Ni, V, Fe, Cu, Pt) of various catalysts,[30] vanadium, nickel, and iron in fuel oils and charging stocks,[31] using a preliminary ashing procedure, and the determination of calcium, barium, and zinc in lubricating oils by direct examination of the oil.[32] This technique, in contrast to that of optical emission, may be applied to continuous process analyses.

Another X-ray analytical technique which is receiving some attention is that of X-ray absorption spectrometry.[33] It has the advantage over both the fluorescence and optical emission methods that it is not subject to matrix effects, and is therefore preferable to the other techniques for work at high element concentrations.

Light Scattering

The increased use of cracked gas oil as diesel fuel has brought with it the problem of predicting the storage stability of such fuels. The ability of submicroscopic particles in a medium to scatter the light passing through it in all directions seems to offer a solution to this problem. For very small particles of random distribution in size, the light scattering is fairly uniform in all directions, but as the particles grow in size they tend to scatter light more intensely in the forward direction. The presence and growth of the particulate matter responsible for instability may therefore be detected by light scattering measurements long before they may be detected by visual or other means. A technique [24] has been developed for predicting the storage stability of diesel fuels, and results obtained to date tend to confirm the value of the light scattering technique for this type of work, for which a British instrument is now available, Fig 4. Apart from its application to diesel oils, the light scattering technique might also be applied to the

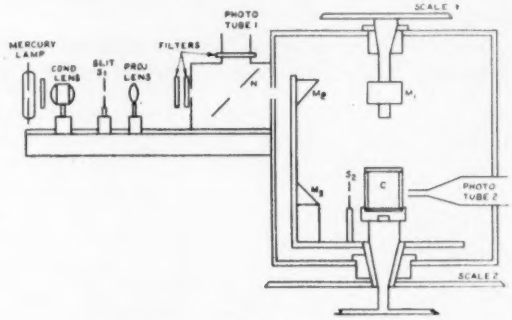

FIG 4
LIGHT-SCATTERING APPARATUS

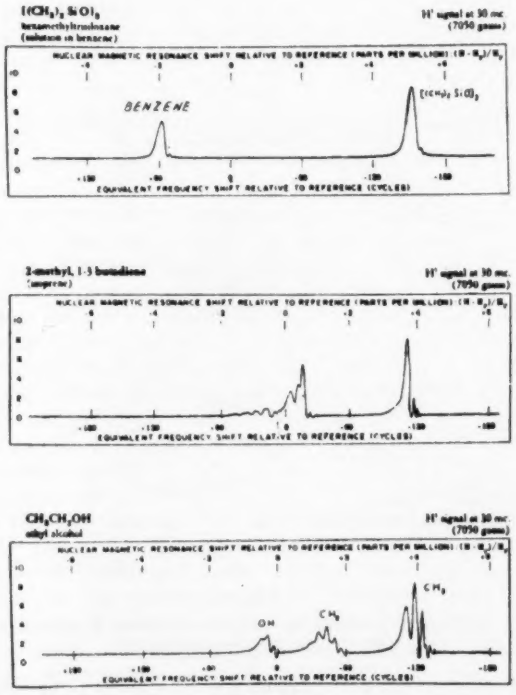

FIG 5

assessment of fuel oil stability and, in the research field, to gum and precipitate formation in gasoline.

A similar approach to the assessment of the stability of petroleum products is one involving the use of a spectro-photometer for the measurement of opacity or, more precisely, the measurement of the total loss of light by scattering in passing through a medium of known thickness.[25]

Electrochemical Analysis

Electrochemical methods of analysis are being used on an ever-increasing scale, and many investigational programmes are either already in progress or planned on new techniques or on modifications of existing ones.

(1) *Polarography.* The polarograph has for years been in use for inorganic analysis. It has dealt with a large number of analytical problems, and much attention has been given in recent years to the polarography of various sulphur compounds.[34-38] Recently, even in this long-established technique, further progress has been made, and polarographs are now available[39,40] having many advantages over their predecessors. One worthy of investigation and likely to increase the value of polarography in petroleum analysis is the Square Wave Polarograph. In this, a small alternating square wave potential is superimposed on the changing potential applied to the cell and, by means of suitable electronic circuitry, all but the desired reaction component of the cell current is removed from the recorded polarogram, which is a derivative type and consists of a series of peaks occurring at the half-wave potentials of the various ions. Some of its applications have been published,[41] but its main advantages for metal ions analysis over the conventional type of polarograph are:

(*a*) greater sensitivity;
(*b*) less chemical pretreatment;
(*c*) simultaneous determination of several constituents can be made even when their concentrations are vastly different.

It is claimed that the square wave polarograph which is now available commercially will determine reversibly reducible ions down to concentrations of 2×10^{-7} N, and the sensitivity of the method is not greatly influenced by the presence of large concentrations of ions that produce interfering waves on the conventional type of polarogram.

The anodic stripping technique and that of "chronopotentiometry" or "voltametry at constant current" are now receiving attention from the point of view of trace element analysis.[42,43] With the former, the element is first deposited on the electrode by electrolysis and then determined quantitatively by a reversed polarographic procedure.[44] In chronopotentiometry the electrolysis is carried out at constant current and the voltage time curve recorded, the time interval over which the voltage remains constant being proportional to the concentration of the element.

(2) *Titrimetry.* The trend in volumetric analyses which forms an essential part of petroleum analysis is to make more use of electrical methods. These include potentiometric, amperometric, and coulometric procedures, and the more recent technique of high frequency titration.

These methods not only circumvent many of the difficulties associated with colour-change end-points, but also have a field of application of their own, in both aqueous and non-aqueous titrations, where suitable colour indicators are not available or where the concentrations of the solutions being titrated are low.

The one in common use is the potentiometric procedure for the determination of mercaptans, acid and base numbers of oils and of nitrogen bases in straight distillates up to and including gas oils.[45] An amperometric method [46] is also being used for the determination of mercaptan sulphur in jet fuels. Automatic titrimeters are now commercially available in Great Britain.

The high frequency technique may become an extremely useful tool because, in contrast to other electrical methods, it does not require the insertion of any electrodes in the liquids under examination. The reaction vessel is placed in a high frequency electrical field where the electric properties of the liquid influence the high frequency current in the system. As the reaction proceeds, the changes in the electrical properties are indicated by a galvanometer or any other suitable recording instrument.

Automatic and Continuous Analysis

Much has been written and said in recent years about automation and the part it will play in future industrial process operation, but it is not generally appreciated that it has already found its way into the analytical laboratory and that, with the increased use of physical methods of measurement, many tests in the petroleum industry will in the future be done automatically.

There is a considerable and growing interest in automatic testing equipment, not only for monitoring plant streams, but also for laboratory use, and many such instruments are now available. Many of these were originally developed by petroleum companies and subsequently commercialized by various instrument manufacturing companies.

The laboratory instruments include, in addition to quantometers and other spectrometers, ASTM-type distillation equipment,[47] potentiometric and coulometric titrimeters,[48] and high temperature combustion sulphur apparatus, all of which are more or less in common use. Probably the most striking of the automatic laboratory equipment is the high temperature combustion sulphur apparatus, which is capable of handling up to 50 determinations in an eight-hour day. This procedure has been published for information in the 1956 ASTM handbook. Its use is, however, limited to materials boiling above 350° F.

The automatic flash point apparatus is suitable for a go/not go test, and it has been applied successfully to ascertaining whether or not products have become contaminated during loading operations.

The plant type instruments include infra-red and ultra-violet analysers, mass spectrometer monitors,

continuous recording refractometers, flow colorimeters, dielectric constant recorders, continuous flow viscometers, initial boiling point recorders, and vapour pressure equipment. The infra-red analysers appear to be, in general, satisfactory, although some have not been entirely successful, due mainly to the lack of experienced maintenance staff on such equipment. There are three vapour pressure instruments available, one of which is of British manufacture.

Much attention is being paid at the present time to the employment of chromatography for the monitoring of plant streams.

Chromatography

The most outstanding recent development in the field of petroleum analysis since the mass spectrometer is undoubtedly that of gas chromatography. This subject has already been covered by numerous publications and symposia,[49] and even a cursory review of the current literature shows that its potentialities as an analytical tool are tremendous.

Most of the important developments of the technique have taken place during the last five years, and within the foreseeable future the method should be firmly established for gas analysis on a quantitative basis in petroleum laboratories, and commercial instruments will probably be available specially designed for this purpose.

The gas–liquid elution method is at present the most popular, and necessitates comparatively simple apparatus comprising:

(1) A sample introduction system capable of handling very small quantities of sample; usually less than 1 ml of gas or a few micro litres of liquid.

(2) A chromatographic column operating at a fixed constant temperature controlled to 0·1° C in which the components of the sample are separated.

(3) A detector and continuously recording system to measure the concentration or total amount of vapour as it emerges from the column. The most popular detector is the thermal conductivity cell.

(4) A supply of eluent gas which moves the samples through the column at a controlled rate of flow.

The application of the method to gas analysis is simple in that most gas mixtures may be resolved fairly easily and identification of the components presents little difficulty. The main problem is in the design and construction of suitable universal laboratory instruments which are reliable, accurate, and straightforward in operation.

For the analysis of liquid hydrocarbon mixtures the method is in some respects more powerful than in the field of gas analysis. Its speed of operation, combined with a high separation efficiency and ease of interpretation of results, makes possible a new range of analyses on a routine basis with comparatively inexpensive equipment and without necessity for highly trained personnel.

For refinery control purposes it is preferable to develop simple equipment for particular problems rather than attempt to develop the completely versatile universal instrument. For plant purposes, most of the difficulties encountered with process stream monitors should shortly be overcome and satisfactory commercial models made available. With some of the more simple plants, these monitors will eventually become controllers, operating according to a product specification through complex computing systems.

In the research field the most interesting developments will undoubtedly be in new column packings with greater specificity and the application of the very sensitive detectors now becoming available.[50, 51]

Thermal Diffusion

Although the mass spectrometer has undoubtedly become the major analytical tool in the determination of the composition of the higher boiling material, the amount of information that can be obtained will depend to a large extent on the type and degree of separation of the material to be examined prior to mass spectrometric analysis. In addition to the older methods of separation, such as fractional distillation and silica gel adsorption, thermal diffusion will play a very important role.

Electron Microscopy

Interest is again being paid to the possibilities of electron microscopy in the petroleum industry, and many American companies are now using the electron microscope for the examination of greases. It may also prove of value for the assessment of fuel oil stability and of the residual detergency of lubricating oils.

Viscometry

With simple fluids, a single measurement of viscosity made in a capillary or efflux viscometer will serve to describe flow behaviour. Many fluids, however, are not of simple type, and flow properties are complex; therefore the only satisfactory way of characterizing them is by means of curves in which apparent viscosity is plotted against rate of shear or shearing stress. The mathematical analysis of viscosity data for complex systems may be simplified if the material under test is subjected to a uniform rate of shear, but this cannot be accomplished by a capillary viscometer and is difficult to achieve with one of the co-axial cylinder type because the gap must be very small. This difficulty and those of manipulation are overcome to a considerable extent by a cone and

plate instrument. The fluid to be examined (less than 0·5 ml) is sheared between the stationary flat plate and a slightly conical rotating disk driven at controlled speeds ranging from 1 to 1000 rev/min.

Thermocouples embedded in the plate (in direct contact with the fluid) enable temperature measurements to be obtained. The plate is also provided with a jacket through which water at a constant temperature may be circulated. The cone speed is directly proportional to the rate of shear, and the viscous drag on the cone is shown on an indicator unit and is directly proportional to the shearing stress. An infinitely variable rate of shear over a very wide range is provided by electronic control of the motor speed. When the sample fluid is sheared in the narrow symmetrical gap between the cone and the plate, the viscous traction on the cone exerts a torque on a precision electro-mechanical torque dynamometer. This is communicated to an electrical measuring instrument giving clear readings on a finely-divided scale having an actual length of 5 inches and an effective length of 25 inches. This equipment may be taken as a typical example of test method development, the results are accurate and swiftly obtained, no exclusive training in its use is necessary, and it could easily be adapted for plant control and measurements.

Digital Computers

Digital computers are in considerable use in America for the computation of mass spectrometric analysis of gases and liquids, including those in the high molecular weight range. They are also used for calculation of process data and costing, and work is now in progress on setting up linear programming schemes for refinery operations. The scope of these instruments was discussed at an IP Symposium held on 7 November 1956.[52]

Statistics

The detection and correlation of sources of error in analytical procedures has always been a major concern of analytical chemists, but it is only during the last decade that the value of the statistical approach has been generally appreciated. Both ASTM and IP have Statistical Committees charged with the task of examining test methods for petroleum and ascertaining their precision. The work of these committees has already shown many analytical procedures to be of much lower accuracy and repeatability than was previously imagined, and the statisticians have been of great help in designing co-operative test programmes to rectify this state of affairs.

Without a reasonable estimate of the precision of analytical and test methods, the true significance of the experimental results cannot be determined, and it is essential, therefore, to assess the precision of any such method before commissioning it.

DISCUSSION

It will be appreciated from what has been written that the major trend is towards instrumental methods of analysis and testing, each having particular features, such as improved accuracy and/or increased sensitivity, but all having the common advantage, namely the ability to speed up analyses; in many cases analyses may be performed in minutes by the new methods, compared with hours by the older chemical procedures. It would be foolish, however, to think that the days of the classical chemical methods are numbered, and the physicists who in the main have been responsible for the introduction of most of the instrumental methods are the first to appreciate this. Rather, the ultimate solution is the close co-operation of physicist and chemist working as a team, with the object of arriving at the best procedure for every particular analysis.

The increased use of instrumental methods, nevertheless, poses many questions, the most important of these being:

(1) How is the time gained by the use of the modern methods to be used to best advantage?

(2) How are they going to affect staff requirements?

The answer to the first depends very much on the functions of the laboratory. In the routine laboratory of a refinery, in certain circumstances the new methods could reduce manpower requirements, but on the other hand, for the same expenditure of manpower many more results could be obtained in the same space of time. Plant control could thus be based entirely on analytical data, and for many processes this would be invaluable, particularly where the specification demands are rigid or where maximum recovery of a product is of considerable importance.

In research laboratories the modern methods, by virtue of their speed, could be used to provide more analytical data and thus make easier the interpretation of the results of research and development investigations. In addition, because the newer techniques reduce both the manpower cost and elapsed time of analyses, many investigations hitherto not undertaken on the score of these two considerations, cost and speed, can now be contemplated, *e.g.* the element analysis of used oils in investigations on engine wear.

On the question of staff, the main core of the routine analysis staff will, as in the past, be the non-graduated technical assistant, because although many of the instruments may be of rather complicated design and construction, their operation is simple and straightforward and, in many, maintenance also presents no real difficulty. On the other hand, if the maximum value is to be obtained from the introduction of these

new techniques, then it is necessary to have more qualified physicists and chemists in the analytical laboratories so that they can ensure that the greatest possible use is made of the extra data that can be made available and so assist the plant development and research chemist in the interpretation of the results. Further, the qualified analysts can devote more and more time to devising new procedures for the new equipment with the object of providing more or better information to the research and development staff.

It must be appreciated, however, that many of the instruments and techniques referred to are at present of value only in the research or development field, but it must also be realized that the research of to-day will in many cases be the routine of to-morrow.

It will also be appreciated that there are now many methods available for a particular analysis or test. Each has its advantages and disadvantages, and the choice therefore depends on the history and composition of the sample and the information required, *e.g.* gas analyses can now be done by very many methods, including low temperature distillation, mass and infrared spectrometry, and chromatography. One of the future tasks of the staff carrying out analytical research will be to review all these methods and to select the preferred one for a particular analysis in the light of the circumstances obtaining.

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NEW TRENDS IN THE INSTRUMENTATION OF REFINERY PROCESSES *

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SUMMARY

The successful operation of any organization or system requires the correlation of four basic functions: information–communication–evaluation–action.

This paper is concerned with the importance of these functions as applied to process plant control, and considers their effects on trends and developments in instrumentation. A review of current methods of process control will show shortcomings, namely: (1) control of product quality is indirect; (2) faithful performance is required from each individual automatic control loop; (3) introduction of long time delays due to sampling and testing routine; (4) the operator is required to assimilate and relate information from a large number of variables. The elimination of these in the many cases where they are significant calls for a fundamental change in approach to control methods.

The development of new techniques and equipment necessitated by this change is discussed.

The possibility of achieving the objective of a completely automatic plant, including an outline of two principles on which the master controller might work, is considered.

It is concluded that, whether or not the completely automatic plant is achieved, benefits will result if the developments and investigations needed to achieve it are carried out.

INTRODUCTION

INSTRUMENTS and automatic controls have become an integral part of refinery plant equipment, and are essential for the satisfactory operation of many processes.

Modern instruments are well engineered and very reliable as a result of twenty-five years of development and refinement.

It is, however, important to realize that there has been no fundamental change in principle or application since the first satisfactory automatic controller made its appearance in 1930. The use of force balance technique and electronic equipment has improved sensitivity, rate of response, and control, but these techniques are a change in method rather than of basic principles.

It is the purpose of this paper to show that a fundamental change in approach to instrumentation is necessary and indeed essential if many process units are to be operated at maximum efficiency.

Automatic control terminology is probably unfamiliar to those not actively interested in instrumentation, and its use has been avoided as far as possible. It has been essential, however, to refer to " open-loop " and " closed-loop " control systems. These can easily be understood from the schematic diagram, Fig 1, which shows the elements of a " closed-loop " system, where the controller is continuously influenced by the results of its own actions.

Changes in the dependent variable, caused by external disturbances or the movement of the regulator (control valve), are continuously measured and transmitted to the controller (feedback). The controller measures the difference between the measured value and the desired value (error) and takes the required corrective action.

It should be noted that if a human operator were substituted for the controller, the system remains a

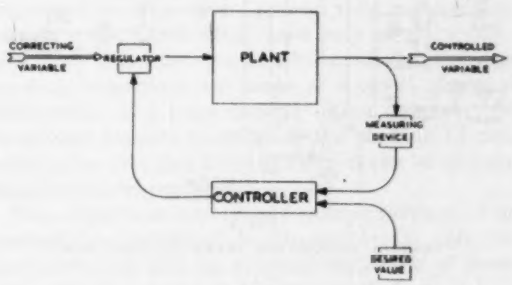

FIG 1
TYPICAL CONTROL LOOP

" closed-loop " so long as the operator is continuously engaged in this particular control function. If, however, the operator were only intermittently employed, the system would be " open-loop " during his absence, and the controlled variable would only remain at the desired value if no disturbance occurred.

PRESENT STATUS OF PROCESS CONTROL

The need for a change in approach to the instrumentation of process units will be apparent if the

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position as it exists to-day is fully appreciated, and it is opportune here to consider the instrumentation of a modern fractionator.

Fig 2 illustrates a conventional control system which has been applied very satisfactorily to a super-fractionator separating *iso*- and *n*-hexane.

It will be seen that the control system consists of a series of individual continuously closed control loops.

The plant operator can and does vary the desired value in the individual loops as necessary to obtain products of the required quality. The product quality is therefore determined by maintaining a number of related variables (pressures, temperatures, flows, etc.) at values found from experience to give an acceptable product.

However, control systems being far from perfect, and being also subject to the effects of disturbances caused by uncontrolled variations in external factors (feed composition, ambient and water temperatures, etc.), it is necessary in practice to confirm that the products are of the required quality by regular laboratory tests.

Reference to Fig 3 will show that the local continuously closed controlled loops form part of two additional loops which are intermittently closed so

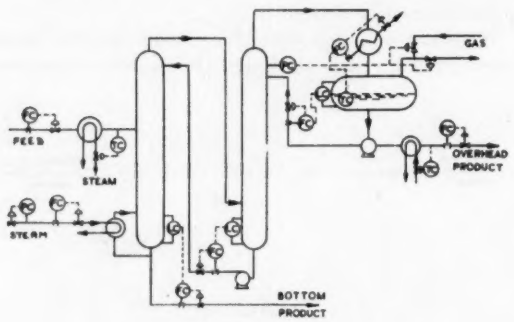

Fig 2

CONTROL SYSTEM FOR SUPER-FRACTIONATOR

that the overall control system of the plant is to all intents and purposes an " open-loop."

In the first, the operator assimilates information from the control panel and takes corrective action and observes its effect on the plant from further observation of the panel.

In the second, the operator assimilates information on actual product quality, obtained from samples drawn from the plant and dispatched to the laboratory for analysis. In some cases a technical department may be brought into the loop for interpretation of results. Final corrective action is again taken by the operator.

The response times of these two loops are markedly different. The first is relatively fast and depends on the skill and vigilance of the operator, and the ease with which he can assimilate the information provided by the instruments.

The second, which is more important, since the information is essential to obtain product quality, is much slower and depends on factors outside the operator's control.

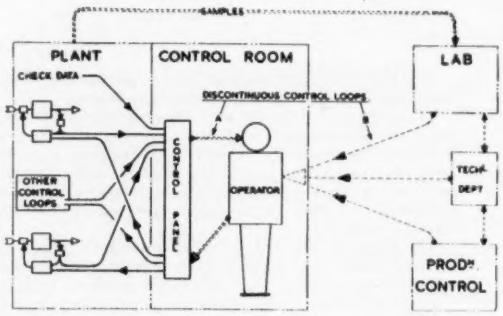

Fig 3

BLOCK DIAGRAM OF A CONVENTIONAL PLANT CONTROL SYSTEM

Fig 3 also demonstrates the information–communication–evaluation–action conception in process control.

The outer loop shows discontinuous samples drawn from the plant (information) transported to the laboratory (communication). After analysis, the results (information) are passed to production control and the operator (communication), who assimilates the results (evaluation) and initiates appropriate corrections (action). Analysis of the individual control loop Fig 1 will show a similar sequence of events, the only difference being that the four functions are carried out automatically and continuously.

It has been shown [1] that long measuring lags are deleterious to good control. An interesting example of the effects of long time lags on product quality and plant efficiency is provided from an analysis of operations of a sulphur recovery plant in the Los Angeles area.[2] Changes made by the operators, on the basis of usual laboratory analysis, sometimes resulted in the plant being operated for long periods under unfavourable conditions with consequent loss of product. Due to fluctuations in feedstock quality, possible errors in chemical tests, and long intervals between such tests, adjustments to controlled variables were often made in the wrong direction.

It is apparent therefore that there are significant shortcomings in present control methods, and these may be summarized as follows:

(1) Control of product quality is indirect.
(2) The method requires faithful performance

from each individual control loop, as one variable out of control will alter the balance of the process. Automatic correlation between other control loops is at present impossible.

(3) Introduction of long time delays due to sampling and testing routine.

(4) The necessity for an operator to assimilate and relate information from a large number of variables.

As a result of providing an operator with more and more information on which to base his actions, there has been a marked increase in expenditure on instrumentation, with little noticeable gain in product yield or quality.

The present method of operation aims at consistent product quality, but it does not follow that consistent quality is either the best or most economical quality.

Plants that have been operating for a considerable time are probably, as a result of trial and error methods, near to optimum conditions, but these conditions may be noticeably different from those at commissioning.

Wiener and Campbell [3] have expressed the opinion that chemical plants, and in particular oil cracking plants, with their part human and part automatic composite control, are reaching the stage where the vicissitudes of human observation and readiness can no longer be relied upon for sufficiently quick response.

It has already been stated that fundamental changes in approach must be made if existing inadequacies are to be eliminated, and there are two important changes which are currently receiving a great deal of attention. These are:

(1) Consideration of the process plant and its control system as an entity.

(2) Consideration of the plant and its control as a unit in a complex economic system. Recent and current developments in instrumentation and control methods such as automatic data logging, quality analysers, electronic control systems, presentation of information, and integration of process plants using computer techniques can be related to these changes.

Impetus to these developments has been given by the emergence of an accepted theory of control and by the control engineer specially trained to apply it.

OBJECTIVES

The new trends in automatic control should enable a process plant to be built and operated to make the most efficient use of raw materials under the most economical conditions, *i.e.* the plant should be capable of operation at optimum conditions.

Assuming establishment of criteria by which optimum operation can be determined (which in itself presents considerable difficulty and involves a number of factors, including market requirements and price levels) the fundamental objective is clearly to build process units which will achieve optimum operation automatically during normal conditions.

Whilst it will no doubt be possible to build a completely automatic plant, defined by Young [4] as " A plant which can be started up by pressing a button and which will continue to operate (in the specified conditions) with maximum efficiency and without human intervention until it is closed down by pressing another button," the desirability of doing so is open to question from both the practical and economic standpoints.

The immediate objectives arising from the above are: (1) the automatic measurement of product quality in the process plant; (2) a detailed knowledge of plant and process characteristics; and (3) the automatic control of product quality which is dependent on objectives (1) and (2) being achieved.

The increasing use of high-speed computers in the planning of refinery operating programmes will involve more frequent changes in plant product quality, and plants and control systems will need to be designed so that they steady out as rapidly as possible after changes of operating conditions.

A general and continuing objective is the improvement of accuracy, reliability, and ease of servicing of instruments.

There is an increasing tendency to place all operating data from a number of process units in a common control room. Individual units may be more complex and, with existing operating methods, decisions on plant conditions are made as a result of visual observation of a large number of instruments. Of immediate concern therefore is the problem of presenting the data in a form in which it can be quickly assimilated and evaluated.

The objectives are largely complementary, and successful achievement is dependent not only on equipment but also on co-operative efforts of those engaged in the design and operation of plant.

PROGRESS TOWARD OBJECTIVES

Determination of Plant Characteristics

The possibility of instability is an inherent characteristic of any control system using feedback (closed-loop), and this possibility increases with increasing complexity of control loops. Consequently, if the " operator " loop is to be permanently closed a very careful study of the system stability is required.

In the general case, analysis of the system is impossible at the present time due to lack of information concerning the plant and process. This is the primary

reason for a forthcoming field investigation into the performance of a particular plant which will be carried out by the authors' company.

It is expected that these investigations will provide sufficient data on the dynamic characteristics of the plant to determine the factors which have the greatest effect on controllability. An attempt will be made to correlate the results with theoretical considerations.

Several techniques are available for the determination of plant dynamic responses, of which the frequency response analysis [5] is probably the most familiar.

Earlier, Ziegler and Nichols [6] developed a method which involved measurement of plant response to a step change in one of the independent variables.

Goodman and Reswick [7] propound the use of normal operating records, and this method has the advantage that it does not involve making an artificial disturbance to the plant. It will, however, be necessary to improve methods, accuracy, and speed of recording data and to ensure accurate synchronization of all records.

MEASUREMENT AND CONTROL OF PRODUCT QUALITY

Before continuous control of product quality is possible new techniques for the automatic analysis of the product must be developed and the reliability and accuracy of existing equipment improved.

It is not sufficient to think in terms of mechanization of laboratory apparatus. For example, the ASTM distillation test can be done automatically,[8] and apparatus is already marketed for this purpose, but it is difficult to industrialize this equipment for plant installation and automatic control, and a new and simple method having direct correlation with ASTM results is required.

Analysers using spectrographic principles have been produced for plant monitoring and control, but those at present available in the U.K. are far from satisfactory.

The recently-developed vapour phase chromatography technique promises to be extremely useful and accurate when specially designed and developed for plant installation. Two such analysers costing about $12,000 each are known to be operating in the U.S.A., and the results obtained have shown a marked increase in plant operating efficiency. A U.K. manufacturer is being encouraged to produce an automatic gas chromatograph which will be installed on a plant to monitor the overhead product and present to the operator a direct record of percentage composition.

It is inevitable that quality analysers will be more elaborate and expensive than conventional plant instruments, due to the high cost of development and the relatively small demand for each type.

As a result, development by the British instrument industry is slow. The situation could be eased if the user contributed to development costs and if joint research organizations undertook such work for their own industry. Large organizations can and should produce equipment for their own specific needs, with the advantage that the instruments would meet the very stringent plant requirements.

The high cost of quality analysers need not, however, be a barrier to their application, as if they were correctly applied, first costs should be quickly recovered in terms of increased yield and plant efficiency. The phrase " correctly applied " is used here to emphasize that a quality analyser should be installed where a significant improvement in plant operation is possible.

It is not uncommon to find that otherwise satisfactory quality analysers are rendered ineffective through inadequate sampling systems, and there is much to be done to improve sampling equipment generally. It is of interest to note that equipment for pipeline sampling is in production by some firms in the U.S.A.

CENTRALIZATION OF INFORMATION AND CONTROL EQUIPMENT

It is common practice in the process industries to group instruments in a central control board to provide operators with an overall picture of plant conditions.

Due to increasing size and complexity of plant, some control boards become so large that it is impossible for any one operator to digest the information presented to him.

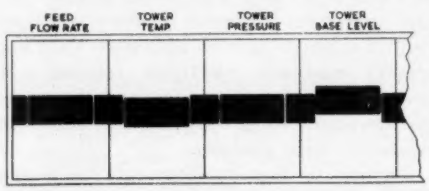

FIG 4

OPERATOR'S VIEW OF AN IN-LINE SCANNER

Reducing the size of the instruments affords some assistance by permitting closer groupings, but in many cases the use of graphic presentation nullifies the expected improvement by scattering interrelated information over the expanse of the panel.

Console type control desks, with all instruments and control stations to hand, are probably the best compromise so long as the standard form of instruments remains in use.

In the functional cycle—information–communication–evaluation–action, communication is probably the most important, since one of the primary problems is getting the information to the right place at the right time.

Indicating and recording instruments in use at the present time are essentially position devices, and the operator is faced with the problem of assimilating and evaluating a large number of analogue values.

Some of the information presented is of doubtful value, and part of it is not available either continuously or at sufficiently frequent intervals.

The continuous indication and recording of variables which are maintained at their correct values is surely unnecessary. The important thing is to draw the operator's attention immediately only to those variables which have deviated from their desired value, and to provide equipment which will show the trend and rate of deviation.

Detailed tests have shown that the ease of scanning a number of instrument dials depends upon the form of presentation.[9] For instance, when the pointers of several circular instruments are all arranged to read at the same cardinal point it is quicker to scan them accurately than if they are arranged at other settings.

A scanning system which makes use of this principle was proposed by Wallis and Simpson,[10] and reference to Fig 4 will show the simplicity of the system.

Internally illuminated edgewise instruments with

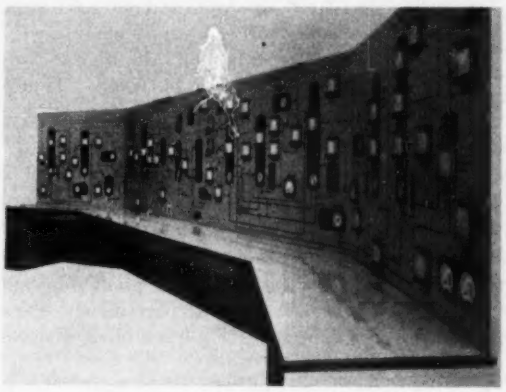

FIG 5 (*a*)

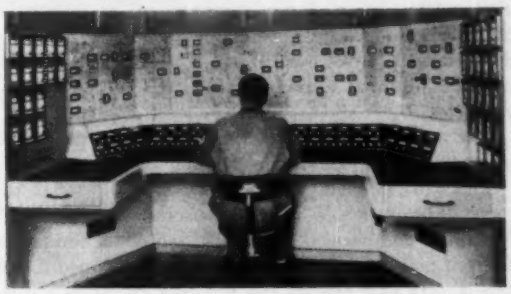

FIG 5 (*b*)

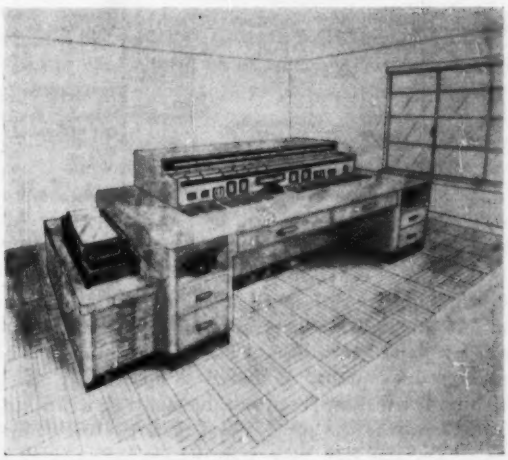

FIG 5 (*c*)

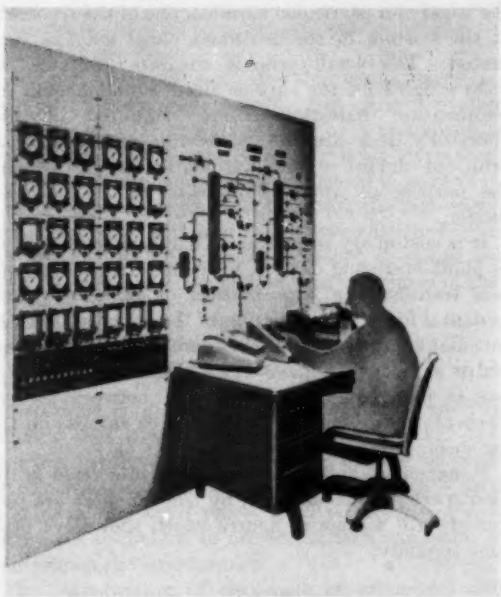

FIG 5 (*d*)

large rectangular pointers are set up in a continuous horizontal line. If the line remains unbroken the plant is stable. Any deviation causes a pointer to move out of line either up or down, depending upon the actuating signal, and is readily detected by the operator.

This arrangement offers a quicker method of evaluating plant conditions than the sequential observation of a large number of conventional indicators and recorders, but since it only indicates deviations from set conditions, it is still necessary to install equipment to record the actual values of plant variables.

The equipment may be conventional recorders and integrators or an automatic logging system.

Figs 5 (*a*), (*b*), and (*c*) show an example of each of the three different types of presentation discussed above, for direct comparison. Fig 5 (*d*) shows a composite form of presentation which has been developed in the U.S.A. In this system the relevant variables are indicated on the miniature circular dial indicators during normal conditions. If the operator wishes to observe the trend of a particular variable, one of the recorders at the bottom of the left-hand panel may be connected. The small graphic diagram contains indicator lights for the various alarm functions and for temperature indicator points. Mounted on the operator's desk are the typewriter and off-normal print-out device of the automatic logging system, the purpose of which is discussed in the following section.

It is customary to produce a handwritten log-sheet of plant operating data at fixed intervals, which entails translating a large number of analogue values to digital form. Compilation of the log-sheet is time-consuming, gives values which are not simultaneous, and is subject to human errors of observation. Upsets in plant conditions can occur between logging intervals which will not necessarily be entered on the log-sheet.

Management and supervisory staff interested in the plant performance as given by the log-sheet are presented with a mass of figures which they have little time to study.

DATA REDUCTION AND COMPUTING

Automatic logging is a better method of obtaining plant values than manual logging and will obviate the necessity of using a large number of recorders.

The design of any specific data reduction equipment will be largely influenced by the purpose for which the data is required. As applied to process plant it is considered that the three main purposes are:

(1) To give a printed record of the time and magnitude of all deviations of variables outside predetermined acceptable limits.

(2) To record automatically in digital form all process measurements required for plant analysis purposes at regular intervals or on demand, and deviations from permitted tolerances at any time. For this purpose the equipment incorporates a scanner which samples all variables in rotation at a speed sufficiently high for the readings to be regarded as simultaneous. Measurements are printed on prepared log-sheets and manual logging of process variables can be entirely eliminated.

(3) To record automatically in digital form data required for accounting purposes. Typical records would include throughput and yield of process units, tank farm stocks, chemical stocks, etc., and these would, where necessary, be corrected to standard conditions.

It is easy to visualize the value of information produced from (2) above to research stations engaged on the evaluation of processes in the pilot plant stage and parailel work on full-scale plant, particularly where new processes are involved. Fig 6 is a block diagram

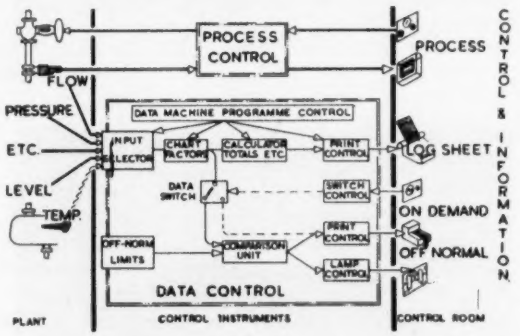

FIG 6

PLANT CONTROL WITH AUTOMATIC DATA REDUCTION

showing equipment applied to a process plant. On the left are indicated typical plant variables to be measured and controlled. The most important of these, product quality, is not listed specifically, since only in a few instances is a suitable analyser available. In the centre is the process and data control equipment. On the right the information actually provided in the control room for the operator is indicated.

Briefly the operation of the data reduction section is as follows:

Off-normal—the input selector normally continuously scans or selects each variable in a predetermined order in rotation, the variable being connected to the data equipment for a sufficient length of time for the value to be measured and the appropriate chart factor for type, *i.e.* pressure, flow, temperature, etc., and range to be applied and for the measured value to be compared with fixed pre-set

values representing the normal high and low limits of the particular variable.

If the measured value is outside the normal limits, the point identification number, time, value, and direction, *i.e.* high or low, are printed in red on the off-normal printer and the appropriate alarm light in the graphic diagram illuminated. The selector then moves to the next variable, and this cycle is repeated. If, when the selector returns to the off-normal variable, it is still off-normal, no print-out occurs. If it has returned within the normal zone, point identification time, value, and a symbol indicating normal are printed in black. No print-out occurs when the selected variable is within normal limits.

Routine log—at pre-set intervals, say every 2 hours, the value of all variables is printed out on a prepared log-sheet by a typewriter, normal values in black and off-normal in red. Where required, computations, *e.g.* for correction of integrated flows, are automatically carried out before printing.

It should be borne in mind that much of the information is redundant unless the actual normal values are required for a specific purpose.

On demand—facilities are provided for any variable to be checked individually at any time.

During the next decade it is quite possible that the control loop will be closed without a human operator being required for evaluation and action, and existing systems of visual presentation of analogue values rendered unnecessary by the substitution of a " master controller " which will automatically absorb all data, and compute and initiate the appropriate corrective actions.

There will obviously be an intermediate stage when special purpose computers are used on certain sections of the plant.

A computer has been defined [11] as " A box whose output or outputs depend on the values of two or more inputs."

It is often the case that in a process, the parameter which best describes its operation cannot be measured directly, but can be defined mathematically in terms of two or more directly measurable factors.

Where the relationship is clearly defined, it is possible to determine the value of parameter with a special purpose computer. This has the advantages of giving the key parameter directly and automatically and of reducing the amount of data to be absorbed. For example, if in a heat exchanger the key parameter is the rate of heat transfer, this can be computed from measurements of the inlet and outlet temperature, mass flow, and knowledge of the specific heat of flowing medium.

An instrument designed for this particular application has been described by Hannula.[12]

One of the principal factors which prevents the general application of computers to automatic process control is the lack of data on plant characteristics, but much can be learnt by using both digital and analogue computers in the study of process plant and control system behaviour.

The trend is to think in terms of optimum operation of plant as distinct from consistent operation.

Optimum operation depends on a large number of factors, such as market requirements and prices, distribution costs, type of crude available, oil stocks, and storage facilities, etc.

The relationships between these factors are complicated, and their determination involves the processing of a large amount of data, much of it statistical. This type of calculation can be done very quickly on digital computers.

Similarly, the equations governing the behaviour of many process plants, particularly those involving catalytic reactions, are complex, and the labour of solving them manually for small changes in each significant variable is in most cases prohibitive.

Gee *et al.*[13] have quoted a particular case in which a series of calculations on a digital computer indicated that a change in operating conditions in a reactor could increase the yield by 15–20 per cent, and an increase of this magnitude was subsequently achieved in practice.

It is not, of course, suggested that similar large improvements are always possible, but quite a modest increase in yield from a large plant or of an expensive product may well give a rapid return on investment in the extra equipment and effort needed to achieve it.

Even with existing forms of control, the high-speed digital computer will help to improve efficiency, as it will provide the information on which decisions are based more quickly, accurately, and in greater detail.

CONTROL MEDIUMS. PNEUMATIC OR ELECTRONIC?

Electronic controls are being increasingly used in industry, but it should be re-emphasized that this does not involve any fundamental change to plant instrumentation, but that a different medium is used to achieve the same result. All electronic process controllers at present in use are in fact analogues of their pneumatic counterparts.

The introduction of electronic measurement and control has some importance, since there are several immediate advantages to be gained and one feature which will have far-reaching effects on future developments.

The true electronic controller with no mechanical parts has less dead zone than pneumatic instruments and responds to much smaller changes in the measured variable.[14] The virtual absence of transmission lags with electrical systems will give better control performance, and the equipment can be installed in any central position for operating and maintenance purposes without impairing the degree of control.

E

It is the flexibility of electrical circuitry which offers the greatest advantage. Whilst computing can be done pneumatically, it is much easier and simpler to do it electrically, and an all-electric system is readily adapted to computer control.

The measurement of gas flow can be taken as an example. Measurements of orifice differential head, gas pressure, and gas temperature in the form of electrical signals can be transmitted to a small analogue calculator which will give a continuous electrical output signal proportional to gas flow corrected to standard measurement conditions. This output can then operate a standard recorder or integrator or be transmitted to a data processing system.

The application of computers to plant analysis, discussed elsewhere in this paper, can be facilitated if the values of the variables involved in a particular test can be produced automatically in the form of punched cards or magnetic tape for direct input to a computer. This can be done easily only by electrical methods.

THE MASTER CONTROLLED SYSTEM

It would be unwise at this juncture to predict the form a master controller will eventually assume, but undoubtedly a computer will be required, and there are two obvious ways in which it might be included in the control system.

The first is in effect to substitute a computer for the human operator, in which case each of the controlled variables on the plant will remain as at present. The computer will receive information concerning conditions in various parts of the plant, including feed and product qualities, calculate corrections, and adjust the individual controller desired values accordingly.

In the second method, which should offer economies in first cost, the computer could be substituted both for the human operator and the individual controllers and, acting as a controller, send out signals direct to the regulating units. Where process conditions do not fluctuate rapidly, it is conceivable that a single computer could be used for a complete plant. Each variable could be sampled in rotation, the regulators being maintained in fixed positions, and adjusted at intervals as decided by the computer evaluation.

The first method, which is an extension to the present system of control, will probably be more acceptable to operating personnel, since, in the event of computer failure, the plant could be operated conventionally.

The computer could be either analogue or digital, but the principle on which it would work is open to question.

If all information concerning plant characteristics, control equipment, etc., could be predicted with sufficient accuracy, the computer could calculate optimum conditions and act accordingly. Alternatively, if the information is not of the required accuracy, the computer might operate in much the same way as the human operator, on a combination of trial and error and past experience.

Machines operating in this way, variously known as maze runners, mechanical rats, and goal-seeking machines, have already been constructed. They are capable of finding a way to a centre or goal by trial and error on the first occasion, and by stored past experience on subsequent occasions. The most advanced machine not only learns simple mazes, but takes advantage of short cuts. It can also learn two mazes and, when these have a common point, find its way to either of the goals on demand.

It would seem therefore that a computer controller could be designed to operate on similar principles. The goal would be maximum efficiency, maximum yield, minimum allowable product quality, etc., and, acting on information fed in from various parts of the plant and from outside, it would carry out a series of trial and error experiments until the desired " goal " was reached. Subsequently, if faced with the same conditions, it would be able to reach the " goal " directly.

The " master controlled " system must be able to take care of abnormal conditions. For example, the computer should be capable of detecting false information caused by faulty measuring equipment, transmitters, etc., since it would not be acceptable to shut down plant for minor instrument or pump failures. This implies that a considerable amount of duplicate instrument equipment will be needed, together with means for automatic changeover and the automatic starting of stand-by pumps. The adoption of telecommunication practice, whereby a certain percentage of equipment common to all circuits is carried as spare and automatically switched in on failure of the working equipment, could meet this requirement, but there is no doubt that the overall equipment would be bulky and complicated.

CONCLUSIONS

The new approach to process control implies that the ultimate aim should be a fully automatic plant, and this will obviously be possible.

Whether such a plant is economically or operationally desirable will have to be determined on its merits, for it will necessarily be complicated and expensive, and it must therefore offer advantages which could not be achieved by other means.

In the meantime increased knowledge of plant characteristics gained from both full-scale plant and experimental investigations, coupled with the use of newly-designed instruments, will of themselves bring benefits in the form of increased efficiency.

The degree of success in effecting improvements in

automatic process control and refinery instrumentation depends to a large extent on close co-operation between all concerned with plant and process design, operation, and research within individual companies and within the petroleum industry as a whole.

ACKNOWLEDGMENT

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DISCUSSION

Dr G. C. Eltenton: The two papers have established that a very rapid evolution, almost a revolution, has been going on during the last 15 years in our methods of tackling analytical and control problems. The more physical approach has very outstanding advantages, two of which the authors mention—speed and accuracy. Increased accuracy often arises from the fact that these tests are more automatic. Built into each piece of equipment is a large amount of feedback control, thus eliminating much human attention of a dull and repetitive kind which is now known to be very unreliable and productive of error. Another advantage of these methods is their ability, at times, to give information which could not be obtained in any other way. Attention should be drawn to two of the references which have been made, one being Dr Beynon's work on the use of a mass spectrometer for the identification of high molecular weight material, using very high resolution, and the other being O'Neal's work in the U.S.A. on the mass spectrometry of waxes and oils.

It is quite extraordinary how the mass spectrometer has proved to be such an extremely flexible instrument. Whenever it seemed to be coming to the end of its tether, as some people predicted a couple of years ago when vapour phase chromatography came in, it was able to expand itself, and bring in new fields, many of them quite unique and as yet insoluble by other methods of measurement.

The scatterometer, if I can give it that name, was not very easy to understand from the figure. The monitoring photo-cell seemed to be taking the light before it had passed through the sample, which raises the obvious question of how the measuring photo-cell distinguishes between scattering and colour changes?

Turning to other points in the first paper, I have been surprised that the overtone region of the spectrum has received so little attention. Yet it has such obvious advantages for automatic measurement in that one does not have to dilute the sample, window materials are simple, and resolution with gratings can be very high. What is the snag? Is it that when using liquids the resolution is limited, not by the apparatus, but by broadening of the absorption lines?

Lastly I should like a little guidance from the same authors as to how they choose between several alternative methods. For example, calcium in lubricating oils can be measured by sulphated ash, versenate, flame photometer, or emission spectrometer. Which is the most accurate and what other criteria enter in the decision?

Yet another advantage of the physical methods is that they lend themselves much mor[illegible] to automatic measurement and control of plants. T[illegible] is brings me to the second paper, which stressed, and quite rightly, that whilst great progress has been made in our ability to stabilize a plant by means of conventional instruments, it is not necessarily stabilized at the optimum for quality and economy of product. I agree wholeheartedly with Mr Townend that more analytical control instruments are needed, but I would question whether their introduction need await that "detailed knowledge of plant and process characteristics" which he implies is necessary. Most plants can be made to run reasonably steadily, but the feedback of information on quality of production is antiquated in its standards of accuracy and speed.

Secondly, I should like Mr Townend's views on whether we shall have to attempt the measurement of feed variables. Changes in these can cause major difficulties in present control, but analysis of feeds, however desirable, will be very difficult in practice.

Turning to that part of the paper which looks at the role of computers in plant control of the future, it would be a bold critic who said, "It can't be done," but the difficulties are enormous. The most intriguing possibility is the scheme whereby we let the computer play games with the plant, gradually increasing its own experience until, like a Pavlovian dog, it can hardly make a mistake. If this were possible many of the painstaking investigations of plant characteristics would presumably be unnecessary. The computer would find them out *en passant*. However, what courage will be required before anyone is prepared to hand over an expensive plant to an inexperienced "electronic operator"! Are any half-way stages being tried, such as controlling an electronic analogue of a plant, or a pilot plant?

In conclusion, I should like to congratulate the authors on the facility of their expositions and the timeliness of these summaries. Although they were dealing with extremely intricate yet elegant machines, which the petroleum industry is, in general, taking in its stride, it was pleasant to see that the human element, the question of staff to understand and run these machines, was not forgotten. Serious thought must obviously be given to the training and status of the specialists required.

Dr H. Powell: Replying to Dr Eltenton's question on the light scattering apparatus, photo-tube 1 in the diagrammatic sketch shown in the paper measures only the energy reflected from the edges of the mirror N and is used to monitor the constancy of emission of the source. The main portion of the light beam passes through the central aperture in N on to the mirror, M_1, and thence via the periscope arrangement, M_2/M_3, into the sample cell, C. The energy scattered by the sample is measured by photo-tube 2, which is fixed in position, the angle at which the measurement is made being determined by the settings of M_1 and the periscope, the angular setting of the latter (scale 2) being twice that of M_1 (scale 1). In applying the light scattering technique to the prediction of storage stability of fuels, the measurements involve determining the ratios of the energies scattered at angles of 45° and 135° to the energy at zero angle. Unless, therefore, the sample is highly absorbing and thus makes measurements of scattered radiation difficult, the colour of the sample is unimportant. For measurements at zero angle the standard apparatus illustrated in the paper has had to be modified by the introduction of an additional periscope so that the beam first passes through it before falling on to M_1. It then follows the same path through M_2/M_3 as previously, but the position of M_2 is lower than that shown in the diagram.

On the subject of the overtone region, I, too, have been surprised that it has not been fully exploited, because it certainly has many advantages over the fingerprint region (5–15 μ) of the infra-red spectrum, particularly for automatic continuous measurements. However, appreciably more sample is required for measurements in this region, and therefore, for research work, where the amount of material available may be small, this could be a serious limitation. That it has not been used very extensively to date is, I feel, due to the fact that most industrial laboratories have been so heavily engaged in using the longer wavelength region and have been loth to inter-change prisms on an extensively calibrated instrument because of the possible risk of upsetting calibrations. This is certainly true of our own laboratory. With the newer instruments, however, the overtone region will, I feel sure, receive much more attention, and it is understood that a number of laboratories are now engaged on investigational work in this region. We certainly propose to examine its potentialities very thoroughly, and in fact it has recently been found extremely useful in deciding the structure of a compound when the normal fingerprint region had failed to provide the complete answer.

With regard to the third question on the choice of analytical methods, the answer depends on a number of considerations, namely, the information required, the type of sample, and speed and accuracy. However, for the determination of calcium in lubricating oils there is little to choose, on the grounds of accuracy, between flame photometry and the direct-reading emission technique referred to in the paper. We prefer the direct-reader for the examination of lubricating oils because it is almost entirely automatic in operation and can be applied to all the elements of interest. The flame photometer, on the other hand, has to be set manually to the appropriate wavelengths and cannot be used for the determination of phosphorus, which is frequently present in lubricating oil additives. The sulphate ash procedure for the determination of lubricating oil additives is very slow by comparison with either of the above spectroscopic procedures, and can only give a figure for the total additives present. Many oil blends contain more than one additive, and in order to obtain the amounts of each additive present it is necessary to determine the concentrations of the elements associated with each additive.

D. S. Townend: The first question relating to our paper concerns the knowledge of plant characteristics. Perhaps we have been guilty of a little over-emphasis. Undoubtedly, the answer to Dr Eltenton's question is that it is not necessary to know plant characteristics before plant analytical instruments can be applied. However, there are advantages in carrying on investigations into these characteristics in parallel with the development of analytical instruments, for two reasons in particular. First, in some cases a greater knowledge of plant characteristics will enable improvement to be made in ordinary environmental control systems. Secondly, in the case of a computer controlled plant with automatic product analysers, once the analyser is connected through a controller to one or more independent variables, a feedback system is produced. It is quite possible for such a system to be unstable or to have a poor dynamic response.

Step-by-step control on a plant which settles down fairly quickly after a change is a compromise. Here the analyser takes a sample, analyses it, and, if off specification, makes a small adjustment and then waits for the results of its action. This sequence is repeated until the product quality is brought within specific action tolerance. It is thus possible to a limited extent to get round a lack of knowledge on plant characteristics. However, while there is much talk about dynamic characteristics it must not be forgotten that steady state characteristics are still very imperfectly known.

I think that feed quality analysers will definitely be required. In the petroleum industry feed analysis often presents a greater problem than product analysis, as the feed is often a complex mixture. It is of interest that some work we have been doing, details of which are not yet available, suggests that the product of a certain plant does vary periodically with the feed.

J. H. G. Carlile: The authors of the first paper indicate that there will continue to be a need for the analytical chemist in petroleum laboratories. I am inclined to disagree, at least in regard to what may be termed the conventional analyst. It appears to me that the chemical work would fall mainly into two classes, one calling for an intelligent observer and the other for a highly skilled specialist. In neither case would the normal graduate chemist be suitably employed. I would suggest that the classical methods of training chemists need drastic revision and would be glad to hear the authors' views on this subject.

With reference to the second paper, is it correct to assume that the authors refer largely to semi-automatic control? Presumably an operator is always at hand to cope with an emergency. In a fully automatic plant it would be necessary to incorporate appropriate " loss of control " switches, so that in the event of a power or mechanical failure, or the faulty functioning of any of

the control loops, the necessary valves would be closed in order to shut the plant down in a safe condition. Incorporation of such safeguards would make the instrumentation highly complex; moreover, the plant would probably shut itself down more often than if an operator was present to take over if an instrument failed.

W. H. Thomas: The point which Mr Carlile has raised is indeed an important one and one to which a great deal of consideration has been given. It is true that to the uninitiated we may be replacing the analytical chemist by a black box with its row of dials and electronic controls. This view is incorrect: we shall always require highly trained analytical chemists who can advise the physicist with regard to the duties of the black box. We must know, for example, what the interfering elements would be in certain estimations. Of paramount importance, also, is the fact that the analytical chemist will always be required on the interpretation of results.

The automatic type of equipment enables us to get more information much quicker than before. That in itself produces further problems for the analytical chemist and we do not anticipate ever dispensing with these extremely valuable people.

Those of us who are closely concerned with such matters are of the firm opinion that universities should have Chairs of Analytical Chemistry in order to ensure the production of an adequate number of fundamentally trained analytical chemists.

D. S. Townend: We have referred in the paper to both semi-automatic and completely automatic control systems. It is felt that development will proceed in stages. It is difficult to visualize anyone designing a " press-button " automatic plant from scratch without any intermediate stages. Probably the first step will be to apply a quality analyser to a conventional plant, in conjunction with an optimizing computer which will have control during normal operation only. Manual operation would be necessary at other times.

It is quite probable that the completely automatic plant will not be a conventional one. Certainly the complications and problems involved in making, for instance, a modern petroleum chemical plant completely automatic are formidable. As Mr Carlile points out, " loss of control " switches would be required, and this aspect is quite as important as that of normal control. Such switches are already in use to a limited extent on many existing units. It would, in general, be unacceptable for a main refinery processing unit to shut down for a trivial instrument fault. The choice of a plant for completely automatic control will have to be very carefully considered.

V. Biske: It would be most helpful to have an economic assessment of some of these new methods. For instance, the determination of sulphur can be done with the aid of X-rays or else by the older classical combustion method; similarly, carbon–hydrogen ratio can be measured by β-ray absorption or, again, by combustion. If one has 20 sulphur tests to do in a day, then presumably the X-ray method is the more economical; if one does one sulphur test a week, then obviously one would not equip a laboratory with X-ray equipment for this purpose. Could the authors give some approximate indication at what point, taken as number and frequency of analyses, modern physical methods, using specialized and perhaps expensive equipment but, I believe, without the need for very highly skilled operatives, begin to pay as compared with the classical slower chemical methods, employing simple apparatus but requiring a relatively more skilled staff.

W. H. Thomas: Mr Biske has raised a question which has naturally been put to us from time to time and fortunately we have been able to prove that the money was well worth spending. Here are two examples of the expenditure of what might be regarded as a comparatively small sum. A small flame photometer was bought for about £100. It was required to do many estimations of the salt content of crude oil. In under a week we had done that work in something like a tenth of the time it would have taken by the classical zinc uranyl acetate method. The second case involved a sum of considerably greater magnitude, some £6000 being spent on an emission spectrograph, with automatic recording. It was fitted with automatic means for burning the sample, thus enabling the avoidance of the time-consuming ashing procedure which is normally required. The analysis can thus be done in seven minutes. The task for which we originally obtained this instrument would have required the combined efforts of twenty-three analysts with the appropriate amount of laboratory space. Thus there is little doubt that £6000 was a small sum compared with the tremendous effort which would have been required if the classical method had been used. It must also be remembered that we are only involved in the first cost of instruments of this nature, assuming of course that they work properly, but if an equivalent number of analysts is employed, not only does one pay them their salaries every year, but normally one pays them more each year. It needs little arithmetic to prove the point when some well constructed and really useful types of automatic equipment are involved.

E. R. Amery: I feel that if this totally automatic plant does become possible it will need a system of proving circuitry. As an example, I believe people in the radio relay service have a means of proving automatically whether a main amplifier, feeding a district, is in fact working. If reception ceases, after a predetermined short period a signal is automatically fed into the input of the amplifier, and if it does not appear in correctly amplified form at the output terminals a spare amplifier is automatically switched into service and transmission carries on normally. That is an example of one technique in that field. No doubt this new idea of process control, with the computer taking charge, will demand similar techniques to ensure reliability and continuity of operation. Otherwise, the completely automatic plant will not be a feasible possibility.

Reference has been made to the lack of need for precise knowledge of plant characteristics, and there was mention of this electronic noughts and crosses machine, and the ability to solve mazes and so on. I am rather appalled at the thought of a computer playing noughts and crosses with the various closed loops, each having its own dynamic characteristics and parameters, and I would like to hear further details, if Mr Townend can give them, of how he feels that this can be achieved in practice. Perhaps, first, one would establish an equilibrium formula which would be impressed upon the computer and around which the control equipment would be allowed to search within certain narrow limits, and in a manner related to the relevant time constants.

D. S. Townend: Mr Amery's first point is related to that of " loss of control " switches raised by Mr Carlile.

The provision of spare equipment and automatic routine equipment testing is very likely to be necessary. At present, if one or more instruments fail, the operator can usually keep the plant going temporarily until repairs have been effected. We have not gone into much detail on this as yet, since we are concentrating more on obtaining the data needed before such an automatic plant can be designed.

Incidentally, it is not inconceivable that the computer/controller of an automatic plant will have to carry out its own frequency response or equivalent analysis. It is well known that some plant characteristics change over a period of operation, due, for example, to fouling of heat exchangers.

We agree that any automatic controller based on trial and error operation would have to work within very closely defined limits so that it would not create a dangerous situation, or try to correct a condition not in its power to correct.

The points raised are very difficult and involve looking into the future, and we have considered this aspect in general terms only. We are concentrating on the immediate requirements of quality analysers and plant investigation. One very important factor to bear in mind is that any advanced scheme for automatic control must ultimately be economically justifiable. One great difficulty we find, unlike Mr Thomas, who can quote figures of financial saving, is in trying to assess the potential economic gain to be obtained. It is hoped that before long it will be possible to assess the margin for one particular plant.

A vote of thanks to the authors was accorded with acclamation.

THE MESOMORPHIC BEHAVIOUR OF THE SODIUM AND LITHIUM SOAPS PREPARED FROM OXIDIZED PARAFFIN WAX*

By K. U. INGOLD† and I. E. PUDDINGTON†

SUMMARY

The densities of the anhydrous sodium and lithium soaps, prepared from the acids produced by the oxidation of paraffin wax, have been measured over a temperature range of 25°–320° C. There are only minor discontinuities in the density–temperature relationship compared with those exhibited by the corresponding stearates. It is concluded that this smoother relationship is due to the complex nature of the soaps and is the reason that the soaps make such excellent grease bases.

INTRODUCTION

THE general technique for converting mineral oil products to fatty acids and soaps by air oxidation at an elevated temperature has been known for many years. Various methods of oxidizing paraffin wax were used in Germany during the second world war on a commercial scale, the primary object being soap manufacture.[1] This soap was used partly for lubricating grease manufacture, and recent work has shown that such greases are in certain ways superior to greases made from soaps of animal or vegetable origin.[2–6]

It has been known for some time that when a grease is heated to a temperature at which a phase transition occurs in the soap base there is a change in the soap network spread through the grease, which generally tends to promote bleeding and a reduction in the yield value.[7] A correlation therefore exists between the phase changes occurring in an anhydrous soap and its ability to form greases with flow properties stable over a large temperature range.[8,9] It might, therefore, be expected that the formation of superior greases from oxidized wax is due to a decrease in the number and importance of the phase transitions of the anhydrous wax soaps. The present work deals, therefore, with a dilatometric study of the mesomorphic behaviour of the anhydrous sodium and lithium soaps, prepared from oxidized paraffin wax.

EXPERIMENTAL

A large number of methods have been proposed for oxidizing paraffin wax to fatty acids. In the present work two different methods were chosen in order to see what effect the method of preparation would have on the final soaps. The chief differences between the two methods was the temperature of oxidation and the formation in one case of free fatty acids and, in the other case, of soaps. The oxidation apparatus was similar in both cases. It consisted of a vertical glass column, across the bottom of which was a fritted glass disk through which the air was introduced. The lower part of the column was wound with heating tape and the upper end of the column was open to the atmosphere. The temperature was measured with a mercury thermometer and was controlled to $\pm 2°$ C. A refined paraffin wax (m.p. 56° C) was used throughout these experiments. It was added to the reactor in the molten state together with the catalyst, the temperature was then raised to the required value, and the air blown through the mixture.

The first oxidation procedure, by which soaps are formed directly, was a modification of Fischer's method,[10] which eliminated the necessity for working above atmospheric pressure. Some 2–10 per cent of a finely divided alkaline substance such as Na metal, NaOH, Na_2CO_3, $LiOH.H_2O$, etc., was added to the molten paraffin. Na metal was added as an emulsion in the molten wax, and water-soluble alkalis were added as aqueous solutions to the wax at 150° C so that the water evaporated rapidly and left the alkali in a finely divided state.

Alkali inhibits the reaction,[10–14] and it is therefore necessary to work at fairly high temperatures (180°–260° C). One advantage of this technique is that neutralization of the carboxylic acids prevents the formation of esters, lactones, and anhydrides. The soaps formed can be separated from their mixture with unoxidized wax and neutral oxidation products by several methods, such as extraction with water or organic solvents, or by centrifuging the hot mixture. In general, the mixture was extracted with petroleum ether until all the wax and neutral products were removed. To remove excess alkali the soap was then dissolved in hot water, acidified, and the liberated fatty acids were separated with ethyl ether. The ether was evaporated and the characteristics of the acids, such as molecular weight, iodine number, and hydroxyl number, were determined. The acids were converted to soaps for dilatometric study by dissolving in alcohol and titrating with alcoholic NaOH or LiOH with phenolphthalein as the indicator. The soaps were crystallized from alcohol and dried.[15]

The second method for preparing the acids was the same as that described by Pardun and Kuchinka.[16] $KMnO_4$ (0·20 per cent) was dissolved in acetone and

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added to the molten wax at the temperature of oxidation (120° C). After the oxidation was complete, the raw product was refluxed with an excess of alcoholic KOH for one hour, the alcohol was evaporated, and the mixture of soap and wax treated as described previously.

The mesomorphic behaviour of the anhydrous soaps was studied using the dilatometric method of Benton *et al.*[9] A weighed quantity of soap was introduced into a J-shaped dilatometer, which was then heated and evacuated to a pressure not exceeding 10^{-5} mm Hg and, after cooling, mercury was admitted to fill the dilatometer. The lithium soaps were fused under vacuum at 230° C, but it was found that a small portion of the sodium soaps decomposed above 240° C, whereas the bulk of the soap did not melt until a temperature of about 320° C was reached. Dilatometric measurements on sodium soaps were, therefore, made on samples given three different heat treatments. In the first case, a sample was fused under vacuum by heating to 320° C for a short period; secondly, a sample was heated to 210° C so that no soap would be decomposed; thirdly, a sample was heated to 280° C so that only a part of the unstable soaps would be decomposed. The second and third samples were pressed into pellets before being placed in the dilatometer and, after adding the mercury, the dilatometers were placed in an autoclave and a pressure of 2000 p.s.i. was applied to squeeze the mercury into any unfilled vacuoles remaining in the soap.

The weights of mercury expelled from the dilatometers as the temperature was raised were determined at 5–10° C intervals. Not more than two determinations were made per day, thus permitting the attainment of equilibrium values. After completion of the above measurements, the capillary was broken at the point of exit from the thermostat and the dilatometer containing soap and mercury was weighed. In the case of those sodium soap samples where gas was evolved, the dilatometer was evacuated and refilled with mercury before weighing. The dilatometer was then emptied and finally weighed when completely filled with mercury. The density of a soap at a temperature T was calculated using the equation

$$\text{Density of soap at temp } T = W_s/[W_o/\rho_t - (W_M - W_T)/\rho_T]$$

where W_s = weight of soap; W_o = weight of mercury required to fill dilatometer at temperature t; W_M = weight of mercury in dilatometer with soap at temperature t; W_M = weight of mercury expelled at temperature T ($W_T = 0$ when $t = T$); ρ_t and ρ_T = densities of mercury at t and T. The assumptions thus made are that the expansion of the glass dilatometer and the expansion of the small quantity of mercury in the capillary outside the thermostat are negligible.

TABLE I

Preparation and Properties of the Wax Acids

Run No.	Additive	Additive concn %	Temp °C	Time hr	Acid No. of raw product	Yield acids %	Mol. wt. acids	Iodine No. acids	OH No. of acids
1	Na	8	220	4·5	–	6·5	250	1·5	–
2	Na	5	230	2·3	–	5	301	2·3	0·65
3	Na	10	260	3	–	5	280	2·0	–
4	NaOH	6	225	4·5	–	5·5	250	6·4	1·45
5	$LiOH.H_2O$	3·2	235	2·5	–	4	272	5·0	–
6	None	–	220	4	29	10	322	27·0	–
7	$KMnO_4$	0·20	120	5	10	5·2	266	5·3	0·98
8	$KMnO_4$	0·20	120	15	44	16	246	0·6	0·95

RESULTS AND DISCUSSION

Table I gives some data on the water insoluble and non-volatile acids obtained by different oxidation procedures. With the possible exception of the acids from run 6, the acids were similar in composition to the acids obtained by previous workers, who have shown them to consist largely of straight-chain fatty acids with a certain amount of hydroxy and unsaturated acids.[6, 10, 16, 18–29] The gas evolved by the sodium soaps on heating above 240° C was due to decomposition of the hydroxy acids.[29, 30]

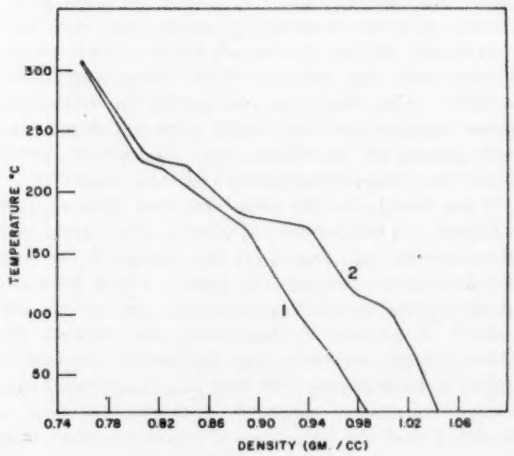

FIG 1

DENSITIES OF LITHIUM SOAPS

1. Lithium wax soaps 2. Lithium stearate

The results of the dilatometric measurements are shown graphically in Figs 1 and 2. The curve for the lithium soap obtained from the acids of run 1 and, for comparison, the curve for lithium stearate, are shown in Fig 1. The results for the sodium soaps are shown in Fig 2 with sodium stearate, sodium 10-methyl stearate, and sodium 12-hydroxy stearate for comparison.[9] As was mentioned above, the sodium soaps started to decompose around 240° C and were, therefore, given different heat treatments under vacuum prior to measurement. The sodium soaps

from run 1 were heated to 320° C, from run 2 to 210° C, and from run 3 to 280° C. The first major discontinuity for each curve occurred at 315°, 232°, and 295° C respectively; they were otherwise coincident within the experimental error. The soaps from runs 7 and 8 were heated to 210° C under vacuum. The first major discontinuity for run 7 occurred at 234° C, but below this temperature the curve was coincident with the curves for the soaps of runs 1, 2, and 3. These four curves have, therefore, been averaged with an error of less than ±0·3 per cent

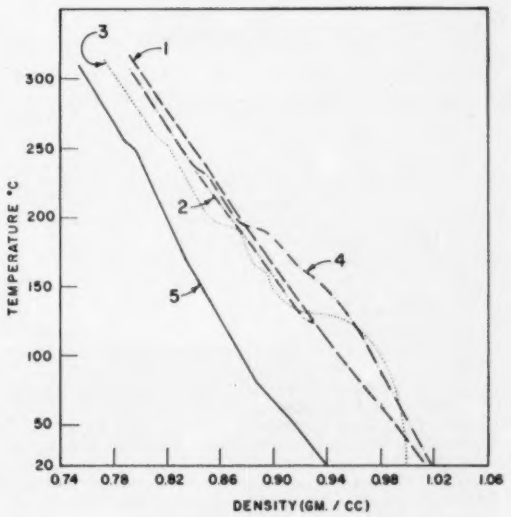

FIG 2

DENSITIES OF SODIUM SOAPS

1. Sodium wax soaps (runs 1, 2, 3, and 7)
2. Sodium wax soaps (run 8)
3. Sodium stearate
4. Sodium 12-hydroxy stearate
5. Sodium 10-methyl stearate

in the density at any one temperature and plotted as a single curve without showing the sudden apparent decreases in density which occur as each sample starts to decompose. It should, perhaps, be emphasized that the volume of gas evolved below 320° C was not large, about 1 or 2 cc/g soap. The soaps from run 8 behaved rather differently. Below 120° C the curve was coincident with the curves for the other soaps, but at this temperature there was a discontinuity. The discontinuity and the remainder of the curve up to the decomposition temperature, 233° C, is shown in Fig 2.

A comparison of the curve for the lithium wax soaps with the curve for lithium stearate shows that there are fewer major discontinuities in the former case. The wax soaps show a minor change of slope at 60°–95° C, a more marked change of slope at 169°–220° C, and a step at 222° C corresponding to the melting point. For comparison, lithium stearate shows three gross discontinuities involving steps in the curve at 110°, 175°, and 225° C. (Compare also lithium palmitate,[31] which shows similar discontinuities at 103°, 190°, and 223° C.)

The curve obtained with the sodium soaps from runs 1, 2, 3, and 7 is very nearly a straight line up to the various decomposition temperatures of the soaps. A close examination shows that there are minor changes of slope from 50° to 110° C, possibly from 180° to 200° C, and from 240° to 290° C. The curve for the soaps from run 8 shows, in addition, a small but definite step at 122° C. It is difficult to explain the different behaviour of this soap, but it must presumably be associated with the greater degree of oxidation of the wax.

The results obtained by Benton *et al.*[8, 9] on the mesomorphic behaviour of a series of substituted stearic acids indicate that the introduction of substituent groups into the hydrocarbon chain of sodium stearate greatly reduces the gross discontinuities in the density–temperature relationship. At first sight, therefore, the density–temperature relation for the wax soaps might be attributed to a high degree of branching of the wax acids. However, analysis of refined paraffin wax [32, 33] has shown that only 8–10 per cent consists of branched chain hydrocarbons, and the hydroxyl numbers given in Table I (assuming one hydroxyl group per molecule [29]) show that only about 12–20 per cent of the wax soaps contain a hydroxyl group. Therefore the wax soaps should contain some 8–10 per cent of soaps with properties similar to sodium 10-methyl stearate and 12–20 per cent of soaps similar to sodium 12-hydroxy stearate. The density–temperature curve for a soap mixture consisting of 75 per cent sodium stearate, 15 per cent sodium 12-hydroxy stearate, and 10 per cent sodium 10-methyl stearate is shown in Fig 3. It can be seen that although the mixture has a low density because of the branched acids, its phase transitions correspond to the phase transitions of the major component, sodium stearate. On the other hand, the discontinuities in the density–temperature relation for a soap mixture containing equal amounts of the sodium salts of stearic, myristic, lauric, pelargonic, and enanthic acids are smaller in magnitude and occur at lower temperatures than the discontinuities of the component soaps (Fig 3), even though the soaps of a series of straight-chain fatty acids behave in a much more similar manner [34] than do the soaps of the straight- and branched-chain acids. Furthermore, the mixed straight-chain soaps maintain the high density of the pure straight-chain soaps. It may be added that the elimination of the phase transitions is not due to the absence of transitions in the soaps with an odd number of carbon atoms: measurements on sodium pelargonate showed that its transitions were similar to the transitions of sodium caprylate and sodium caprate.[34]

The absence of discontinuities in the wax soaps must therefore be attributed to the fact that the soap is not a pure compound, but is instead a mixture of a large number of fatty acid, and substituted fatty acid, soaps of chain lengths sufficiently varied to eliminate or reduce to small areas some of the structural cleavage planes which permit the extensive molecular realignments observed as phase transitions in the pure soaps. The effects which are observed, and appear as small changes in the slope of the density–temperature curves spread over considerable temperature ranges, can be understood as an integrated result of overlapped microscopic phase transitions in diversified highly localized regions. These changes of slope approximately correspond to the temperature ranges

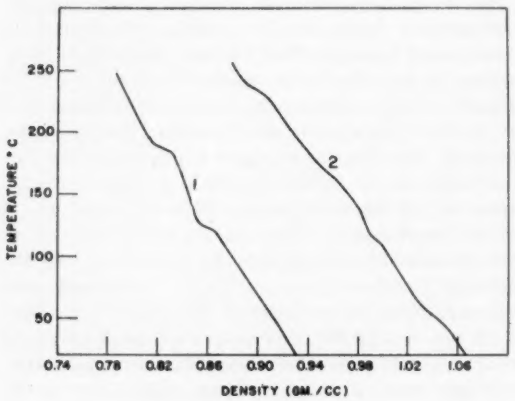

FIG 3

DENSITIES OF SODIUM SOAPS

1. Soap mixture containing 75 per cent sodium stearate, 15 per cent sodium 12-hydroxy stearate, and 10 per cent sodium 10-methyl stearate.

2. Soap mixture containing 20 per cent sodium stearate, 20 per cent sodium myristate, 20 per cent sodium laurate, 20 per cent sodium pelargonate, and 20 per cent sodium enanthate.

marked out by the temperatures of the major transitions of the pure straight-chain soaps.

In order to compare roughly the greases formed by the wax soaps with the greases formed by the stearates, some lithium and sodium greases (9 per cent soap, 91 per cent oil) were prepared with a mineral oil having a viscosity of 300 s.s.u. at 100° F and a viscosity index of 40, and their drip points were measured. The greases were prepared by dispersing the soaps in the oil as far as possible by heating, and then running the dispersion three times through a colloid mill. The wax soaps did not dissolve very easily in the oil, but they were dispersed readily enough by the mill. The drip points were for lithium wax soaps, 180° C; lithium stearate, 155° C; sodium wax soaps, 190° C; and for sodium stearate, 170° C. The higher drip points for the greases made from the wax soaps show that they should operate usefully over a larger temperature range than the stearates.

It should be noted that these greases were prepared from soaps of the water insoluble and non-volatile acids only. It would be expected that greases with even better characteristics should be obtained by using a still more complex soap mixture and it has, in fact, been observed [3] that further improvement in the high temperature properties of the greases can be obtained by using all the acids from oxidized paraffin wax, instead of just the high molecular weight acids.

ACKNOWLEDGMENTS

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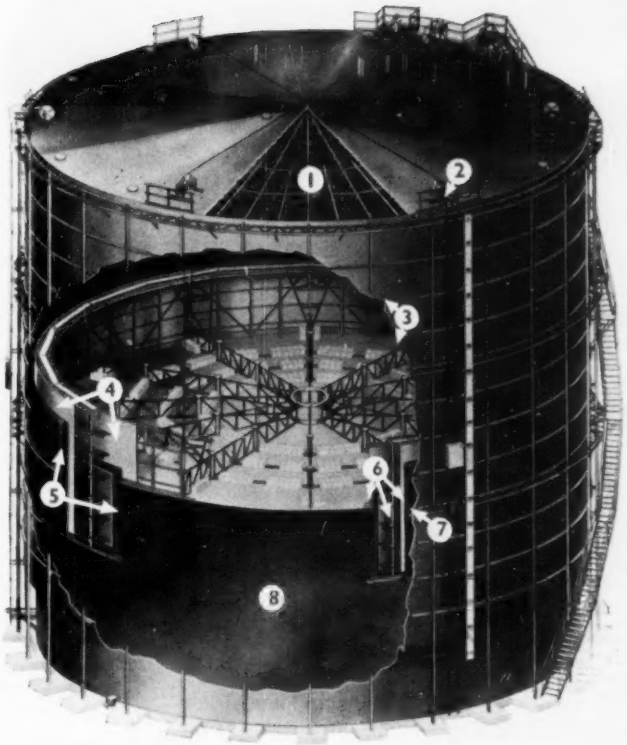

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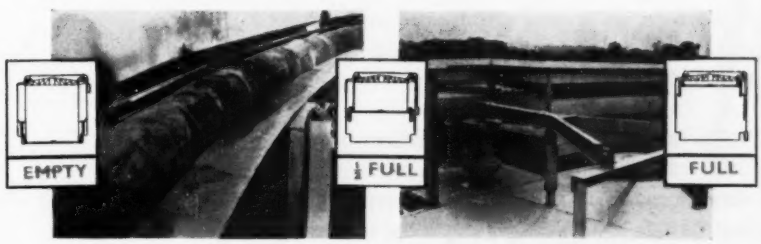

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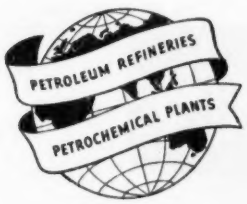

Cut out for the job!

Tightening the bolts on to a "Klingerit 1000" joint ring fitted to the head of a Reactor in the Polymerisation Plant at the Esso Refinery, Fawley (Photograph by kind permission of the Esso Petroleum Co. Ltd.)

Klingerit 1000

JOINTINGS

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G25/58/1

BABCOCK

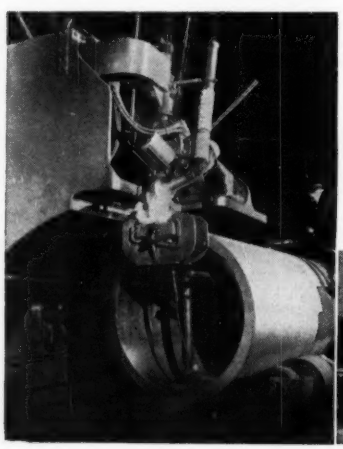
versatile FUSION WELDING

Bottom Right

A Babcock fusion-welded treating tower prior to despatch from the Company's Renfrew Works, for installation at an oil refinery.

Below

Automatic fusion-welding of a thick-walled pressure vessel at Renfrew Works.



The 75 ft.-long by 10 ft.-diameter pressure vessel shown above during installation at the Patchway Works of Bristol Aero-Engines Limited, is part of a special test cell nearly 90 ft. long fabricated by Babcock & Wilcox Ltd. in molybdenum steel, by the *BABCOCK fusion-welding process.*

Designed for the testing of ramjet and turbojet engines, this impressive test plant reproduces simultaneously the conditions of high air speed and low atmospheric pressures associated with high-altitude and supersonic flight.

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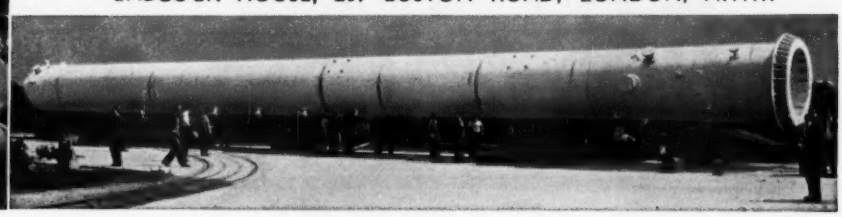
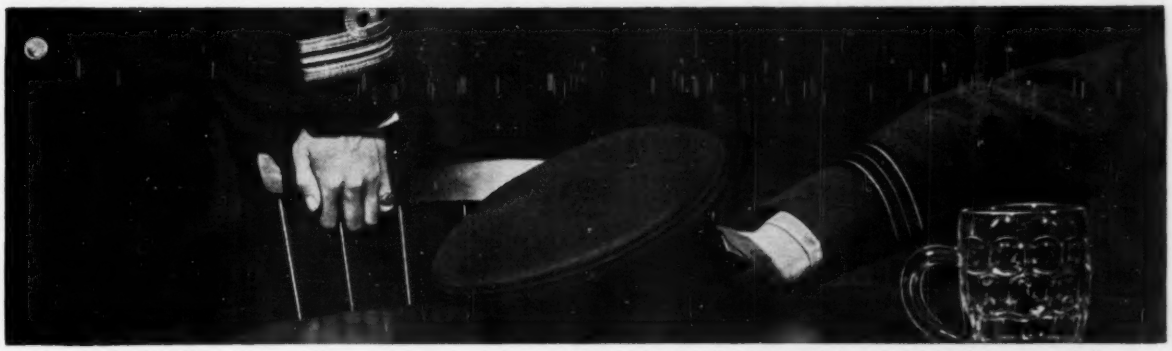
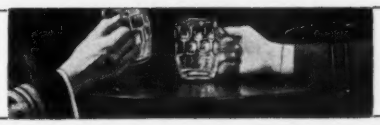


I'm fed up with filters!
let's sit down...



Let's sit down and talk about cricket, the weather... anything so long as it isn't your confounded Simmonds Fram Separators.

Sorry old man... didn't mean to bore you.



That's quite all right. Delighted to know the R.A.F. is getting up to date. So you actually fly your planes on kerosene now instead of water!

Very comical! Anyway, it's not the whole point. I admit the main object of Simmonds Fram Separators is to remove all the water, but they also take out the solids.

Little strips of erk, for instance?

... Anything down to 5 microns.

That gives me a big kick.
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There you are. Now if we could persuade Sally to fit Simmonds Water Separators to the barrels...

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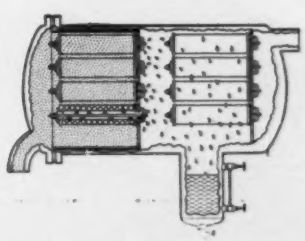

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In the extreme foreground are the cooling tower and blowdown facilities. Intermediate storage tankage is shown in the foreground.

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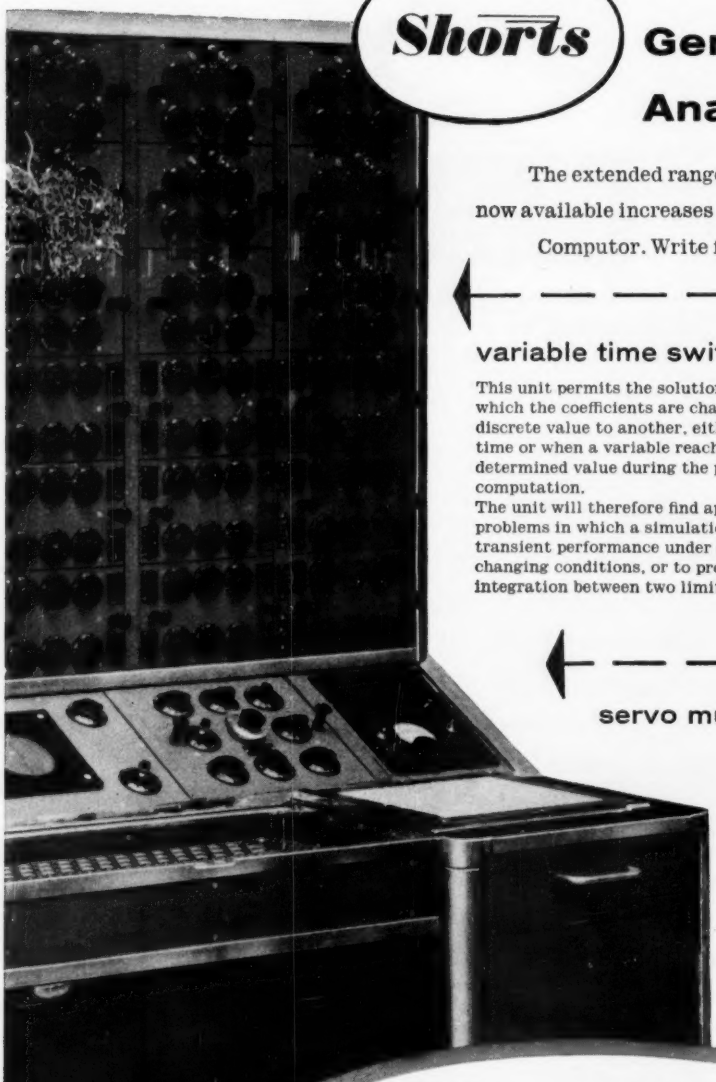

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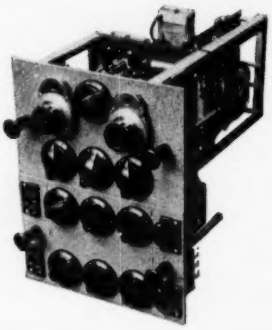

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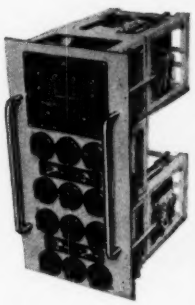

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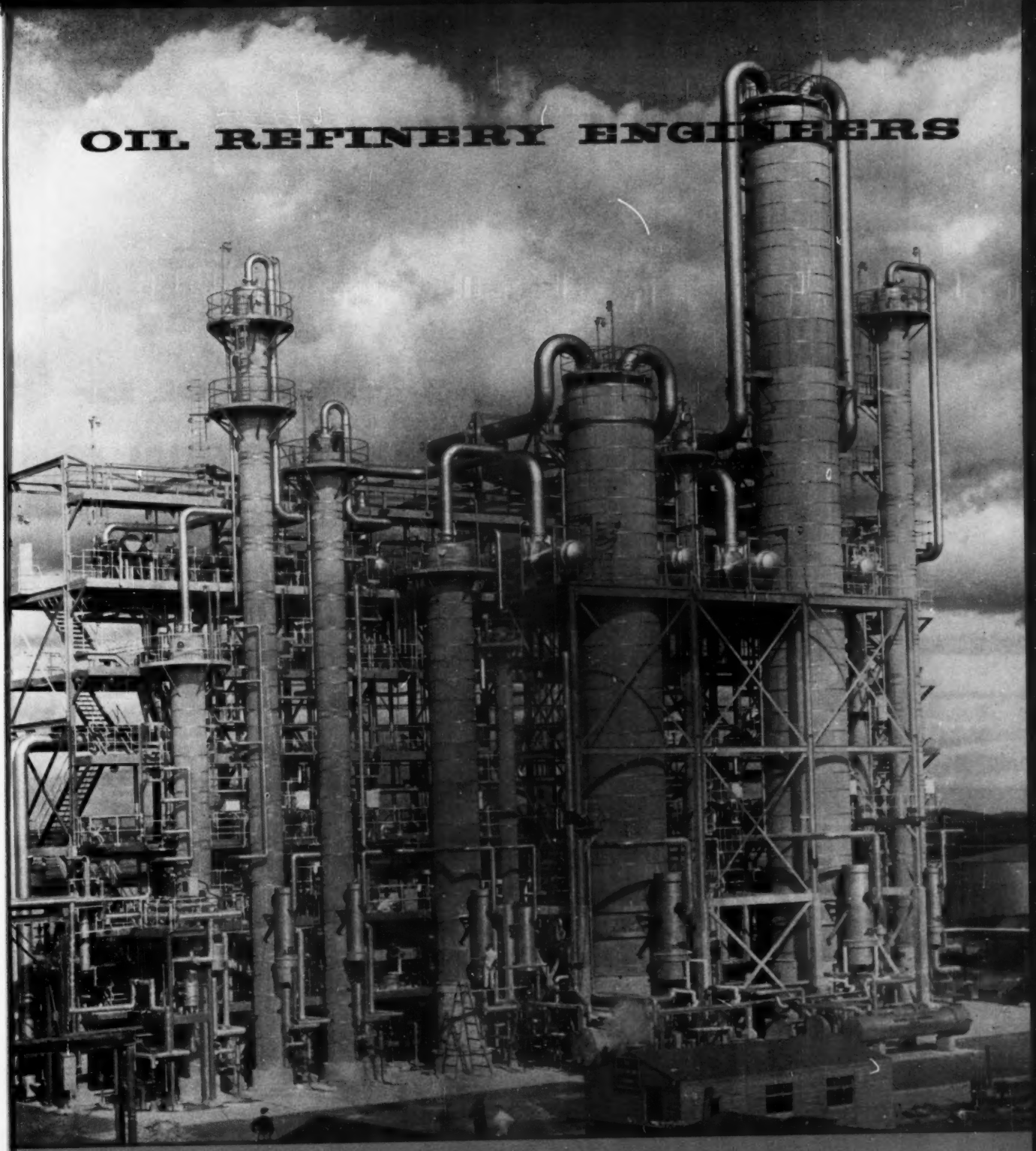

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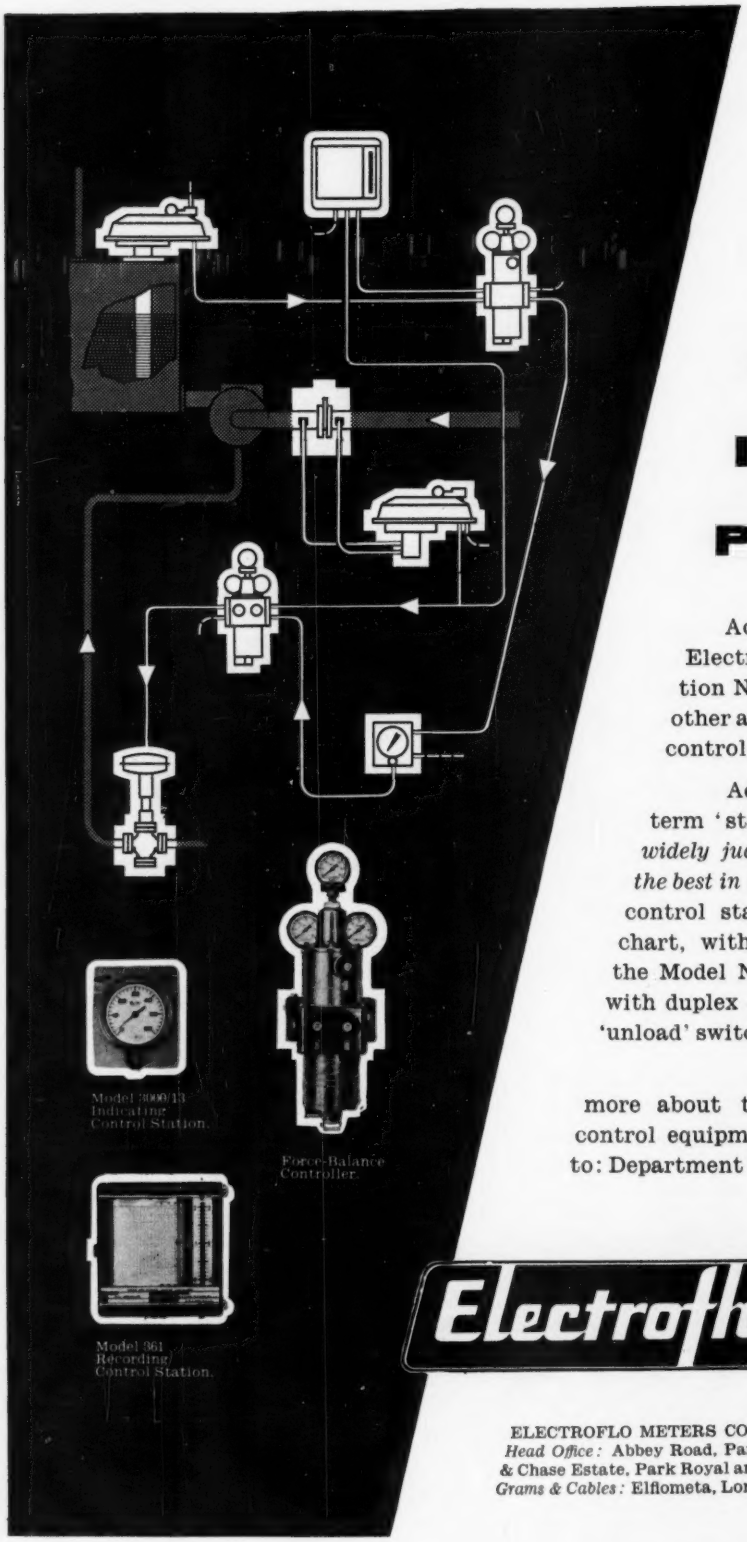

FORCE-BALANCE CONTROL for INDUSTRIAL PROCESSES

Accompanying diagram shows a typical Electroflo cascade control system. Publication No. 90 gives further details of this and other applications of Electroflo force-balance control for industry. Ask for your copy.

Adjoining illustrations show the multi-term 'stack' type force-balance controller—*widely judged by independent evaluations to be the best in its class*—the Model No. 361 recording/control station with 4″ wide rectangular strip chart, with automatic chart economiser, and the Model No. 3000/13 indicating control station, with duplex gauge, automatic/manual switch and 'unload' switch position.

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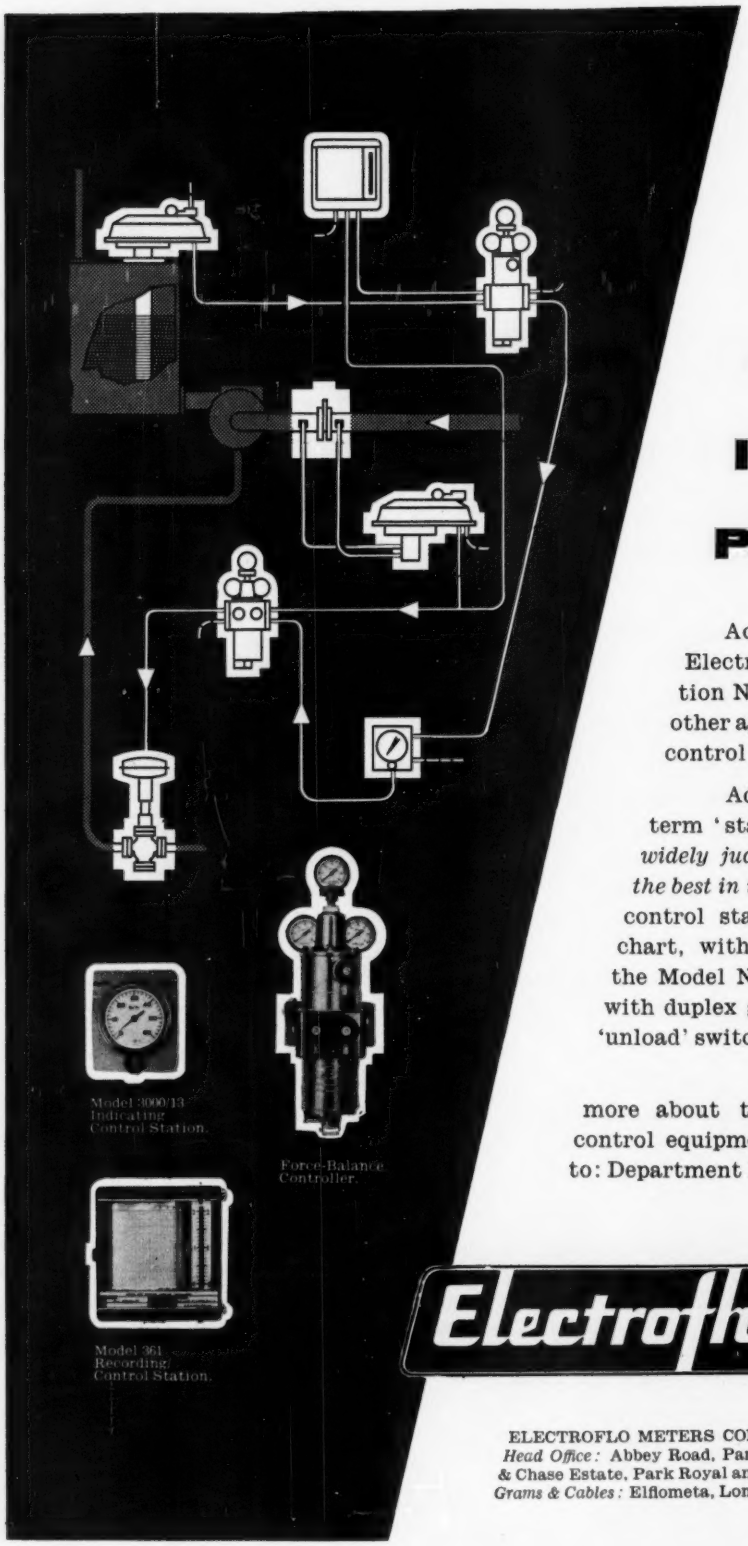

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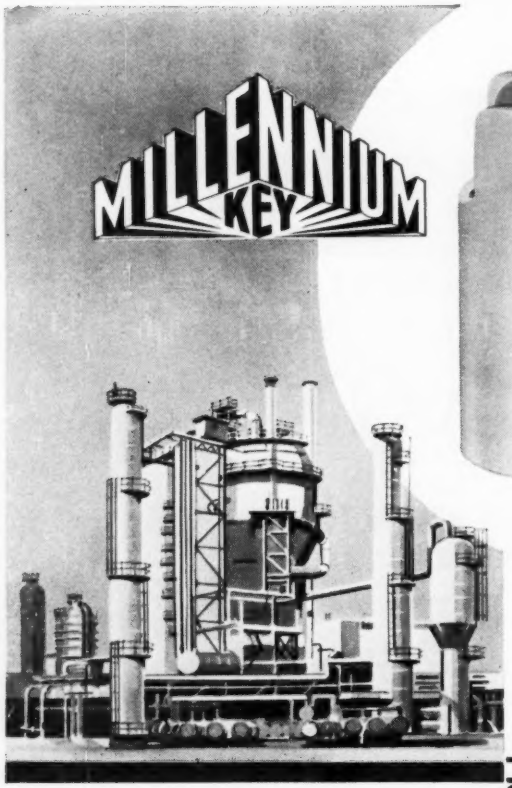

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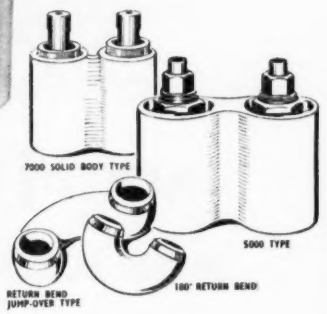

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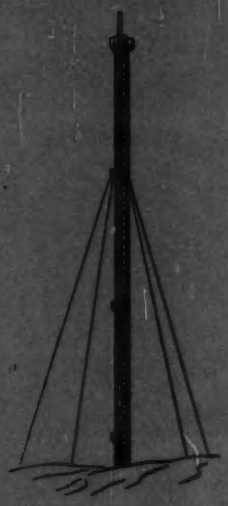
NIMONIC DS

After trials with various materials, Nimonic DS was specified for this new design of flare tip, fabricated by Wilding Technical Services Ltd. to the design of the British Petroleum Co., which is the subject of a Patent Application.



The flare stack is one of the items of plant that the oil refinery engineer would like to fit and forget. Unfortunately, the severe conditions at the tip where waste gases are burned present considerable difficulties which put a limit on life. The temperature of the flare tip varies with the volume of gases exhausted, their calorific value and the temperature and velocity of the prevailing wind. These conditions are aggravated by the tendency of the flame to sweep downwards around the outer lee side of the tip. From the fact that even from the ground it can be seen to be glowing red, it is believed that at times the temperature may reach 800°C. As a result of trials with various materials at the B.P. Group's Llandarcy refinery, Nimonic DS was selected for a new design of flare tip. This nickel-chromium alloy has good resistance to both oxidizing and reducing atmospheres and retains much of its strength at temperatures up to 960°C.

WIGGIN NICKEL ALLOYS

Full details of these flare stack tips are given in No. 42 of our technical publication, Wiggin Nickel Alloys. Please write for a free copy.

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